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PB-259 919

Removal of Soluble BOD(5) in Primary Clarifiers

Institute of Paper Chemistry, Appleton, Wis

Prepared for

Industrial Environmental Research Lab, Cincinnati, Ohio

Sep 76

328050

PB 259 919

EPA-600/2-76-221
September 1976

Environmental Protection Technology Series

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TECHNICAL REPORT DATA
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1. REPORT NO. EPA-600/2-76-221

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE REMOVAL OF SOLUBLE BOD_5 IN PRIMARY CLARIFIERS

5. REPORT DATE September 1976 (Issuing Date)

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) George A. Dubey, Averill J. Wiley, John W. Collins

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Effluent Processes Group
The Institute of Paper Chemistry
Appleton, Wisconsin 54911

10. PROGRAM ELEMENT NO. 1BB610

11. CONTRACT/GRANT NO. R-803119

12. SPONSORING AGENCY NAME AND ADDRESS

Industrial Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED Final 7/20/74-9/30/75

14. SPONSORING AGENCY CODE EPA-ORD

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This project was directed to evaluating means for increasing BOD removal from primary treatment systems treating pulp and paper wastes. An improved understanding of the optimal conditions for soluble and colloidal BOD removal should permit increasing efficiency in total organic removal.

The initial phase surveyed 12 mills to obtain data on total and soluble BOD_5, COD, suspended solids and color removal from sedimentation systems. This data was used to select mill effluents for additional study. These laboratory studies showed that, with proper flocculating agents, soluble BOD removal could be markedly increased. Soluble BOD was defined as that organic load passing through a 0.45 μm filter. micrometer

Measurement of sludge volumes and sludge dewatering characteristics produced from use of iron salts, alum and polymers was outside the objective of the study.

Gel chromatography studies showed that low molecular weight biodegradable residues and colloidal materials were flocculated and removed. Studies with model compounds indicated that increased removal is apparently related to pH of the solution and to functional groups, chain length, branching and solubility of the compound.

Chemical costs may range from 3¢ to 10¢ per 1000 gallons. Cost reduction and improved clarifier performance can be achieved by elimination of overflows and spills within the mill that are antagonistic to efficient sedimentation due to dispersant action.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Precipitation (chemistry) Coagulation Flocculating Oxygen demand	Primary treatment Water pollution control Pulp waste treatment Paper waste treatment Chemical degradation	13B

18. DISTRIBUTION STATEMENT Release to Public	**19. SECURITY CLASS** *(This Report)* UNCLASSIFIED	**21. NO. OF PAGES** 155
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	**22. PRICE** 6.75

EPA-600/2-76-221
September 1976

REMOVAL OF SOLUBLE BOD_5 IN PRIMARY CLARIFIERS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Removal of soluble BOD_5 in primary clarifiers presents research findings related to means and methods for improving the efficiency of primary sedimentation systems treating pulp and paper wastes. The possibility of greater BOD removal was investigated by examining effects of flocculants and coagulants in removing soluble and colloidal constituents of such wastes. The report also discloses that certain process waste streams may be antagonistic to efficient sedimentation and should be treated separately from total mill wastes. This information will be of interest to segments of the industry wishing to upgrade primary treatment efficiency to reduce loadings on secondary treatment. The findings are also applicable to treatment of waste streams not containing significant additives, as the tissue industry, wherein effluent guide-line allowances may possibly be satisfied by efficient primary treatment. For further information contact the Food and Wood Products Branch, Industrial Environmental Research Laboratory-Cincinnati.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Primary clarifiers used in the pulp and paper industry show wide variations in BOD removal. This project was directed to evaluating means for increasing BOD removal and developing an understanding of the mechanism. Such understanding should permit optimization of BOD removal during primary clarification.

A survey involved twelve mills, nine with primary clarifiers, to obtain data on total and soluble BOD_5, COD, suspended solids, and color. These data were used to select mill effluents for additional study.

Laboratory studies showed that, with the proper flocculating agent and operating conditions, the BOD_5 concentration of some mill effluents could be markedly reduced during clarification. These findings were confirmed by pilot-scale clarifier field trials at two mills.

Measurement of sludge volumes and sludge dewatering characteristics resulting from chemical treatment were outside the objectives of this study.

Gel chromatography studies showed that considerable low molecular weight biodegradable residues along with colloidal material were also flocculated and removed. Studies with model compounds indicated that increased removal is apparently related to the pH of the solution and to the functional groups (hydroxyl, phenolic, and carboxylic), chain length, branching, and solubility of the compound.

Chemical costs may range from 3¢ to 10¢ per 1000 gallons of feed to the clarifier. Decreased cost and increased operating efficiency in total treatment systems, as a result of improved clarification, could more than justify this chemical charge. Minimum levels of chemical costs will depend upon minimizing or eliminating overflows or spills of colloids and dispersants detrimental to clarifier efficiency.

This report was submitted in fulfillment of Project No. R803-119 by The Institute of Paper Chemistry Effluent Processes Group under the partial sponsorship of the Environmental Protection Agency. Work was completed as of August, 1975.

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ACKNOWLEDGEMENTS

The original objectives of this project in terms of evaluating the degree of BOD removal attained in primary clarification of pulp and paper effluent waters were conceived by Dr. Everett Cann of the Wisconsin State Department of Natural Resources. The project was organized and conducted by the staff of The Institute of Paper Chemistry. George Dubey, Project Supervisor, had responsibility for detailing and conducting the laboratory and field studies and for reporting the results of this research in cooperation with Averill Wiley, Project Director, and Hardev Dugal, Director of the Institute's Division of Industrial and Environmental Systems.

Gerald Hovind, Arthur Webb, and Gay Fraundorf were principally involved in the extensive analytical program. The field studies were greatly facilitated by help from John Baumann who installed and operated The Institute of Paper Chemistry pilot equipment, by James Albrecht and Al Kleist of the Mosinee Paper Corporation, and by Lawrence Weyenberg and James Roovers of the Combined Locks plant at National Cash Register.

Ralph H. Scott, Chief of Pulp, Paper and Wood Staff, Food and Wood Products Branch, IERL-Ci, EPA, as Project Officer, has had responsibilities for the immediate supervision of this project in accordance with the objectives of the program.

SECTION I

INTRODUCTION

The overall degree of biochemical oxygen demand (BOD) removal actually observed in most conventional out-plant clarifiers treating total mill effluents has been relatively small (5-15 percent) and has seldom extended to levels that would significantly improve effluent quality. A search of the literature disclosed few published investigations of the mechanisms for the BOD removal in clarifiers. Only two (1,2) gave data indicating possible sources of BOD that is removed during clarification. The State of the Art Review of Pulp and Paper Waste Treatment by Gehm (1) attributes the BOD to "the high content of suspended organics and small quantities of dissolved organic matter" in certain types of waste and to the "fact that the oxygen uptake rate of fiber is slower than that of dissolved materials, since it must first be liquefied before oxidation can take place." Das and Lomas (2) point to glucuronoxylans and araboglucuroxylans as water soluble hemicelluloses (from the beating of pulp) that reduce the BOD when removed with the floc. One of the first goals of Phase I of this research program was, therefore, to evaluate by a controlled analytical study the removal performance for total and "soluble" BOD_5 in different clarifiers at pulp and paper mills. Surveys of mill waste flows and clarifier effluents were conducted at 12 mills owned by 11 companies. The analytical data developed during this survey established the basic program of the investigation and the definitions of the terms "soluble" and "total 5-day biochemical oxygen demand (BOD_5)" to be used throughout the balance of this study.

Three different classes of BOD-forming components in the various waste flows were identified:

1. Substantial quantities of the BOD being removed in clarifiers are obviously suspended fibers and related solids in various stages of physical, chemical, and biological degradation. These suspended particles may originally have low levels of solubility and low BOD but can undergo degradation to produce soluble substances responsible for BOD. This fraction comprises the principal source of BOD readily removed in conventional clarifiers.

2. Advanced degradation of cellulose and hemicellulose particles and the presence of papermaking additives such as starch may provide a substantial amount of soluble, high molecular weight components with biochemical demand for oxygen. Most of these kinds of substances can be surface-adsorbed and removed by advanced clarification procedures. The further development and field testing of routes to removal of this fraction comprised a principal area for development under Phase II of this project.

3. A third fraction of the BOD contained in pulp and paper waste waters is comprised of low molecular weight degradation products of carbohydrates, such as acetic acid, aldehydes and alcohols, which are not readily amenable to physical adsorption and flocculation. Removal of these components has not been reported for primary treatment if we except those cases of prolonged holding time or other conditions where advanced stages of microbiological action are evident in the clarifier.

The fundamental physicochemical mechanisms of flocculation of pulp mill white water fines studied by Williams (3) and the work by Back (4) on the nature of wood components dissolved in the pressure refining of mechanical pulps provide information on a possible approach to the development of an understanding of the mechanisms involved in the removal of BOD components from waste streams. Their ideas were used to develop the jar testing procedures used in our laboratory for the optimization of the removal of BOD_5 constituents from various total mill effluents.

Phase I studies were funded jointly by a group of U.S. pulp and paper companies (Appendix A), the U.S. Environmental Protection Agency (EPA) (Grant No. 803 119), and the Wisconsin Department of Natural Resources (Ref. No. 8100).

For a supplementary and confirming Phase II program, small-scale pilot equipment was used for on-site comparative studies, paralleling commercial clarifiers operating at two mills representative of a broad segment of the pulp and paper industry. Additional funds were supplied by the U.S. Environmental Protection Agency under an extension of the above grant and by The Institute of Paper Chemistry. This confirming program of study was designed to evaluate the operating parameters developed in the earlier Phase I laboratory research under mill conditions. The first trial was conducted at an integrated kraft mill and the second at an integrated mill producing pulp by a recently developed chemimechanical (CM) pulping process.

Laboratory jar tests were also used to evaluate the flocculation and clarification characteristics of individual sewer discharges at these two mills. We studied the effects of processing each of these streams separately and we could also check the effect each had on the overall BOD_5 efficiency of the clarifier when processed as a part of the total mill effluent. Additionally, the jar tests were used to test the removal of soluble model compounds (acetic acid, aromatic dicarboxylic acids, etc.) from solution with the various flocculating agents in order to help elucidate the mechanism of BOD_5 reduction.

An economic evaluation of the data of two field trials and the results of the jar tests conducted on individual streams show the savings which might be realized if the relatively small volumes of stronger pulping effluents, containing lignin compounds with dispersant properties, were not treated in the clarifier.

SECTION II

SUMMARY AND CONCLUSIONS

1. A large portion of the BOD entering the primary clarifiers processing pulp and paper manufacturing waste waters are solubles that can pass through a 0.45 µm filter.

2. These components are generated from wood in pulp and papermaking steps, including wood handling. They may also come from papermaking additives such as starch or sizes. These materials can be degraded within the mill or during out-plant treatment.

3. Laboratory jar tests with various chemical flocculating agents and operating parameters showed that significant quantities, ranging to 20 percent or more, of the soluble BOD_5 and color could be removed from wastes from mills surveyed in Phase I studies. These findings were confirmed by pilot scale field trials at Mosinee Paper Company at Mosinee, Wisconsin, and at the Combined Locks mill of the NCR Corporation in Combined Locks, Wisconsin.

4. Jar tests with the individual waste streams making up the total mill discharge have shown that certain streams contribute both high BOD_5 levels and chemicals that are detrimental to the efficient operation of the clarifiers. Elimination of these streams from the out-plant clarifiers could provide increased quality to the mill discharge. It would also decrease the load on the secondary treatment plant. The streams that were removed from the influent to the clarifier could be treated separately in small clarifiers or by reverse osmosis, ultrafiltration, or other small unit processes.

5. The mechanism for the removal of soluble BOD_5 is very complex due to the heterogeneity of the wastes treated in the clarifiers. There was no apparent relationship between the initial soluble BOD_5 concentration and the ultimate removal of the soluble BOD_5 components by the clarification process.

6. Gel chromatography analysis of effluents before and after coagulation with iron and pulp fines showed a significant number of low molecular weight compounds were removed. Model compound studies showed that many organic acids including some quite soluble could be partially coagulated in an iron-pulp fines system as well as substances which do not form salts with iron.

7. Evaluation of the benefits and costs of achieving improved performance of clarifiers requires detailed engineering studies to fit individual mill situations. Such studies were beyond the scope and objectives of this study. However, it was apparent that total chemical costs, including the chemical additives which may be used in existing practices at these mills,

might range from 3¢ to 10¢ per 1000 gallons treated. Efficient use of these chemicals would be balanced by benefits and cost reductions in the overall systems of waste treatment.

8. Good clarifier performance and low chemical costs could only result from adequate control of mill overflows and spills so that strong colloids or dispersants do not enter the clarifier.

SECTION III

RECOMMENDATIONS

These studies have shown that with the proper selection of flocculating agents and operating conditions, soluble BOD_5 concentrations in waste streams can be markedly reduced (10-50 percent) in the primary clarifier.

Collapse of the double layer surrounding the charged molecule, bridging, and decreased solubility after treatment with the flocculating agent are mechanisms which could be expected to contribute to the removal of both total and soluble BOD_5 components, as well as color, from the effluents.

1. We need to know more about the constituents and characteristics of different kinds of sludges — those from high and low levels of soluble BOD_5 removal — and their effect on the efficiency of clarification in mills processing under different conditions. This could add considerably to our knowledge of the mechanisms involved. The influence of individual mill waste streams in clarifier sludge performance also needs further study.

2. Many of the individual sewer discharges were found to have adverse effects on the efficiency of the clarifiers and also to have a toxic effect on the 5-day BOD test. Removal of these streams from the clarifier inflow could markedly increase the efficiency of both the primary and secondary (biological-type) treatment systems. Diversion of these flows, which are usually of small volume, to other treatment systems is recommended.

3. Selection of the streams to be "eliminated" could be undertaken under laboratory conditions with a combination of jar and BOD_5 tests. Processes for treating the eliminated streams by separate in-plant clarification, reverse osmosis, ultrafiltration, or the training of plant personnel to reduce the discharge of the detrimental stream would follow the identification of these major sources of difficulty.

SECTION IV

MILL SURVEYS

EQUIPMENT AND PROCEDURES

Weekly samples from mills using clarifiers consisted of two gallons of the influent to the clarifier and a single gallon of the clarifier effluent. Where possible, both samples were collected as 24-hour composites. Mills not using clarifiers sent in two gallons of the effluent they were discharging into ponds or aeration lagoons. Table 1 describes the types of mills and their facilities for pulping, bleaching, and effluent treatment; this table is based on data supplied by the mill staff.

As soon as the samples were received in the Institute laboratories at Appleton, Wisconsin, the influent samples were composited, well mixed and immediately transferred to one-gallon plastic bottles. One bottle was filled to the brim, set aside to settle for one hour, and the top 6 inches of supernatant was withdrawn using a light vacuum and a short U-bend at the end of a glass tube. This permitted removal of the top layer of "clear" fluid without drawing the "settled" material from the bottom layer. A second bottle of the influent and also a bottle of clarifier effluent were separately mixed and analyzed "as received."

Samples of the "as received" and "settled" material were pressure filtered through various porosity filters. These filters were 1.2-µm and 0.45-µm pore size Metrical membranes from Gelman Instruments of Ann Arbor, Michigan and a 0.10-µm plastic filter from Nuclepore of Pleasant, California.

Suspended solids, BOD_5, and chemical oxygen demand (COD) were determined on the initial samples and on all fractions.

Samples for suspended solids were processed on 1.2- and 0.45-µm filters on a Gelman pressure funnel at 6.9 kg/cm^2 (100 psig) with N_2 and dried at 103-105°C (218-221°F) for one hour. For biochemical oxygen demand we used the standard APHA Method (5), keeping the samples at 20°C (69°F) in a water bath and determining the dissolved oxygen with a Weston and Stack probe. The COD was determined by the dichromate oxidation method of APHA (6). Color was determined at pH 7.6 using the National Council for Air and Stream Improvement method (20).

Some waste samples filtered slowly through 0.45- and 0.10-µm filters. To avoid filter clogging, a pad of filter aid (Celite, AR, Johns-Manville) was used on 1.2-, 0.45- and 0.10-µm filters for these wastes. The filter-aid pad was formed from a 1-percent slurry of Celite AR poured onto the filters and then dewatered. Analysis of these samples with and without the use of the filter aid (Table 2) indicated that the filter aid did not adversely affect the analytical accuracy. Therefore, in later work, the filter aid was

TABLE 1. DESCRIPTION OF MILLS SURVEYED

Mill	Type of cook	Tons/ day	Bleaching sequence	Effluent sewers	Volume, mgd[a]	Clarifier additives
A	Ammonium bisulfite, aspen	NA	NA[b]	Pulp mill wash water	5.6	Gendriv 162 2 mg/l
B	Acid sulfite	NA	NA	NA		No clarifier
C	Groundwood	225		Coater	0.19	
				Paper machines	2.3	Cationic polymer 1.7 mg/l
				Boiler room & treatment plant	0.2	
D	Acid sulfite (pH 2.5) 66% softwood 34% hardwood	115	Single stage calcium hypochlorite	Evaporator condensate	0.1	None
				Decker	5.0	
				Bleach washer	1.5[c]	
				Paper mill	1.0[d]	
				Miscellaneous	0.4	
E, EE	Kraft, groundwood	NA				No clarifiers
F	Chemimechanical, also NSSC and kraft fibers used in papermaking	350	High density peroxide	Wet room	2.16[e]	None
				CM	1.41	
				No. 6	1.17	
				Main	1.10	
				No. 5	0.53	
				Old filter backwash	0.40[e]	
				New filter backwash	0.43	
G	None-deinking mill	150	C-EH-H at volume ratio 90:5:5	Decker deink	1.2[e]	Anionic polymer 1.5 mg/l
				Bookstock deink	0.8[e]	
				No. 3 & 4 paper machines	0.40[f]	
				No. 5 Peper machine	0.55[f]	
				Beater room additives	0.47[f]	
				Chlorination waste water	0.38	
				Misc. (water treatment plant sludge, etc.)	0.40	

See end of table for footnotes.

TABLE 1 (Continued). DESCRIPTION OF MILLS SURVEYED

Mill	Type of cook	Tons/ day	Bleaching sequence	Effluent sewers	Volume, mgd[a]	Clarifier additives
H	Kraft Pine with 10% hardwood (oak)	370	None	Paper machine	4.5	None
				Salvage filter	4.0	
				Excess screen room white water	4.0	
				Water treatment blowdown	0.6[g]	
				Utilities department	3.0	
				Kinney strainer reject	3.0	
				Hot pond overflow	1.0	
I	Kraft Pine, Douglas-fir, western larch, spruce	1150	CEHD	Clear water	3.5	None
				Pulp mill & recovery	5.0[c]	
				Bleach plant, paper mill & recaustizing	7.3[c,d]	
JJ	Converting mill	205	None	Mill effluent	4.75[h]	None
				Sludge from water treatment	0.08[i]	
J	Groundwood	455	None	Paper machine stock room and coating plant	3.0	Polymer, 0.5 mg/l
				Paper machine	1.5	
				Off-machine coater	0.5	
				Groundwood operation	2.0	
				Cooling & miscellaneous	1.0	
K	Kraft Pine	230	None	Paper machine	10.0[e]	Hercofloc 812.3, 0.75 mg/l
				High density	1.5	
				Pulp mill	0.6	
				Foul evaporator condensate	0.3	
				Soda recovery	0.28	
				Digester blowdown condensate	0.07	
				Digester room	0.05	
				5th Stage brownstock washer	0.04	

[a] mgd = Million gallons per day.
[b] NA = information not available.
[c] Defoamers added.
[d] Pitch control chemical added.
[e] Estimate.
[f] Defoamers and detergent added.
[g] Alum and silicates added.
[h] Wet strength resin, defoamer, talc, animal glue, slimicides, rewetting agent, dryer release, and organic dispersants added.
[i] Alum and chlorine added.

used as a standard practice with the precaution of first checking the effect on one or two samples of each waste stream. Eventually the exploratory studies with various grades of filters resulted in adoption of the 0.45-µm porosity as a standardized procedure.

TABLE 2. ANALYSIS OF FILTRATES PREPARED WITH AND WITHOUT FILTER AID[a]

	BOD_5, mg/l				COD, mg/l			
	1.2 µm[b]		0.45 µm[c]		1.2 µm		0.45 µm	
Sample	With	Without	With	Without	With	Without	With	Without
F	190	178	182	176	464	436	409	369
	74	82	70	80	212	216	199	191
H	32	34	31	32	133	123	108	114
	48	42	44	46	105	126	118	106
B	770	778	672	675	3741	3650	3636	3615
	1246	1230	1218	1184	5363	5320	5190	4890
C	166	192	188	184	352	362	329	329
	184	181	168	174	316	316	275	292

[a] Celite (AR) BOD_5 = 0.04 mg/g.
[b] 1.2-µm BOD_5 = 1.92 mg/sheet.
[c] 0.45-µm BOD_5 = 0.62 mg/sheet.

A few samples were also processed through a Dia-Flo (Amicon Scientific Systems) stirred ultrafiltration (UF) unit with a nominal 100-A (0.01 µm) pore filter. The results were compared with those from the 0.45- and 0.10-µm filters (Table 3). Since no differences were apparent in either BOD_5 or COD, the more time consuming UF procedure was not routinely used.

TABLE 3. COMPARISON OF ULTRAFILTRATES FROM A 100-A MEMBRANE WITH FILTRATES PREPARED WITH FILTER AID OVER 0.45- AND 0.10-µm FILTERS

	BOD, mg/l		
Sample	SUF[a]	S045F	S010F
F	259	310	266
	272	256	267
H	30	43	32
	59	48	50
JJ	40	38	35
	35	40	40

[a] SUF – Dia-Flo stirred ultrafiltration cell with 100-A membrane.

DATA AND DISCUSSION

In order to establish the various total and soluble components of BOD_5, the incoming samples were analyzed "as received," "settled," and after passage through either 1.2-, 0.45-, or 0.10-µm filters (Figure 1). Throughout this section of the report, the designations are as follows:

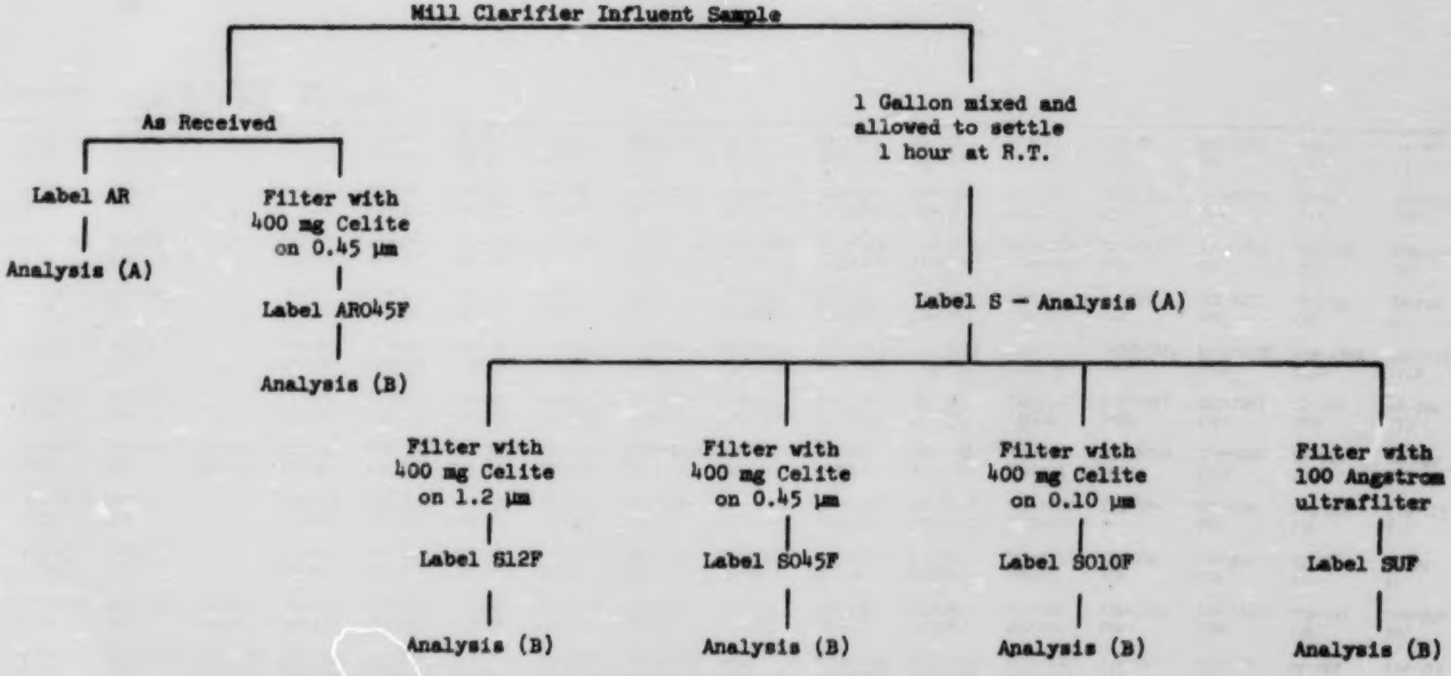
AR	As received
AR045F	As received, filtered through 0.45-µm filter with a Celite overlay
S	Settled
S12	Settled and passed through a 1.2-µm filter
S12F	Same as S12, except with Celite overlay
S045	Settled and passed through a 0.45-µm filter
S045F	Same as S045, except with Celite overlay
S010F	Settled and passed through a 0.01-µm filter with a Celite overlay
SUF	Settled sample filtered through a 100-A UF unit

Data in Table 4 are averages of the six samples from each mill, along with high and low values (range) for each set. The values in parentheses are the percentages of the constituent in the sample after treatment. BOD_5 decreases as filter pore size decreases (Figure 2). The data in Table 4 and Figure 2 can be summarized as follows:

1. Comparing "as received" and "settled" values, we find a marked reduction in BOD_5 (to 62 percent) after simple settling (JJ).
2. The 0.45-µm filter was, for all practical purposes, the best filter for the removal of "insoluble" BOD_5. This filter was used for further studies of "soluble" versus "total" BOD_5.
3. Seven percent additional BOD_5 could be removed from the JJ mill samples by passing them through the 0.45-µm filter.
4. The COD values paralleled, but did not directly correlate with, the BOD_5 values.

In order to evaluate the operation of the mill clarifiers we analyzed clarifier influent and effluent samples in the same manner. Data for these samples "as received," and filtered through 0.45-µm filters, are given in Table 5 (BOD), Table 6 (COD) and Table 7 (suspended solids). In order to simplify the presentation, the "as received" values are plotted in the same sequence in Figures 3, 4, and 5. Marked reduction in total BOD_5 was achieved in clarifier JJ. All clarifiers except those of Mills I and J achieved 50-90 percent removal of suspended solids.

Unfortunately, the values for constituents and removals are quite erratic, probably due to a time lag for arrival of these constituents at the sampling points. Although most samples were 24-hour composites, compensation for the effect of the clarifier "holding time," in some cases on the order of 18 hours and in most cases at least 4 hours, was not built into the sampling system. While this would have little effect on the monthly mill averages, it had a marked effect on the samples sent to our laboratories (Table 8). We found major differences in pH, BOD_5, and COD for the two streams in spite of


Mill Clarifier Influent Sample
As Received
1 Gallon mixed and allowed to settle 1 hour at R.T.
Label AR
Analysis (A)
Filter with 400 mg Celite on 0.45 µm
Label AR045F
Analysis (B)
Label S – Analysis (A)
Filter with 400 mg Celite on 1.2 µm
Label S12F
Analysis (B)
Filter with 400 mg Celite on 0.45 µm
Label S045F
Analysis (B)
Filter with 400 mg Celite on 0.10 µm
Label S010F
Analysis (B)
Filter with 100 Angstrom ultrafilter
Label SUF
Analysis (B)

Analysis (A) – Suspended solids with 1.2 and 0.45 µm, BOD_5 and COD

Analysis (B) – BOD_5 and COD

Figure 1. Schematic for processing clarifier samples for soluble BOD_5 study.

TABLE 4. ANALYTICAL DATA FOR TREATED AND UNTREATED SAMPLES DURING EVALUATION OF METHOD FOR "SOLUBLE" BOD$_5$

Mill		BOD$_5$, mg/l						COD, mg/l					Suspended solids, mg/l			
	pH	AR	AR045F	S	S12F	S045F	S010F	AR	S	S12F	S045F	S010F	AR12	AR045	S12	S045
A	6.68 6.5-6.8	495 358-664	315(64) 215-422	354(71) 254-510	311(63) 231-486	293(59) 232-390	279(56) 214-382	1863 1402-2286	1262(68) 1016-1624	1218(65) 1000-1529	1207(65) 960-1538	1066(57) 892-1396	380 262-524	441 262-548	45 0-70	76 46-96
B	5.00 4.0-9.8	1120 864-1485	1081(96) 602-1359	1076(96) 726-1407	1014(90) 756-1338	938(84) 603-1218	906(81) 552-1231	4860 3660-6140	4548(94) 2457-6000	4370(90) 2127-5765	4347(89) 2150-5880	4032(83) 2132-5355	353 184-824	412 232-872	154 44-260	214 104-314
C	6.98 6.7-7.6	276 222-327	168(61) 108-266	208(75) 128-273	172(63) 112-254	165(60) 108-266	162(59) 100-239	712 608-780	427(60) 313-621	292(41) 215-401	283(40) 188-382	260(36) 171-372	1092 508-1788	1126 752-1780	182 124-241	201 120-280
D	7.20 6.6-8.2	149 100-212		88(59) 51-144	73(49) 30-143	71(48) 28-126	65(44) 24-132	583 477-724	383(66) 310-499	277(47) 182-404	246(42) 175-405	248(42) 167-390	202 124-390	235 154-408	53 32-96	64 50-88
E	4.77 3.4-10.2	490 298-710		456(93) 285-665	451(92) 272-663	424(86) 263-600	412(84) 251-591	2024 940-3494	1523(75) 854-2472	1360(67) 801-2186	1349(67) 801-2186	1250(62) 787-2106	278 138-384	318 192-384	137 108-206	173 128-228
EE	6.16 5.2-6.6	295 156-394	197(67) 182-285	235(80) 125-281	191(65) 119-226	188(64) 112-234	188(64) 112-211	1763 1156-3284	589(33) 442-696	448(25) 304-598	414(23) 302-544	395(22) 309-498	868 136-2110	1218 216-2332	136 36-272	171 90-284
F	5.43 3.6-7.9	359 121-613		197(55) 84-393	154(43) 79-280	147(41) 70-267	140(37) 72-220	1684 802-2268	522(31) 238-762	387(23) 212-527	366(22) 191-508	331(20) 156-472	1097 676-1461	1242 888-1848	110 25-245	115 52-205
G	9.93 6.6-11.5	787 482-927		630(80) 286-847	538(68) 270-692	536(68) 286-711	498(63) 255-687	2918 1702-3990	1821(62) 812-2796	1214(42) 574-1633	1201(41) 574-2565	1146(39) 574-1521	3984 2453-6075	4165 2473-6086	1680 556-2333	1679 520-2573
H	7.46 6.9-8.7	76 44-110		49(64) 26-70	39(52) 27-52	39(52) 28-46	36(47) 24-50	272 174-416	168(62) 102-246	107(39) 83-130	108(49) 73-132	100(37) 75-118	177 97-222	240 182-376	66 36-108	72 38-116
I	8.24 6.5-10.2	622 328-836		575(92) 311-765	432(69) 184-724	404(65) 225-728	409(66) 222-730	2132 1065-3388	1910(90) 914-3195	1668(78) 597-2975	1144(54) 588-2350	1388(65) 491-2495	633 260-1456	853 360-1628	348 164-536	426 198-648
J	8.74 7.0-8.1	230 153-310		204(88) 120-263	132(57) 94-167	134(58) 89-164	136(59) 86-162	715 411-1138	502(70) 357-756	370(52) 275-586	329(46) 259-540	336(47) 278-373	644 270-1034	690 290-1118	337 88-654	365 152-652
JJ	8.02 7.4-8.8	122 69-246		46(38) 30-82	44(36) 30-86	38(31) 26-47	38(31) 32-44	691 404-802	218(32) 86-626	99(14) 71-123	88(13) 65-112	87(13) 64-113	568 386-647	581 409-665	33 8-92	43 14-90

(% Remaining = $\frac{\text{settled (or filtered) value x 100}}{\text{as received value}}$)

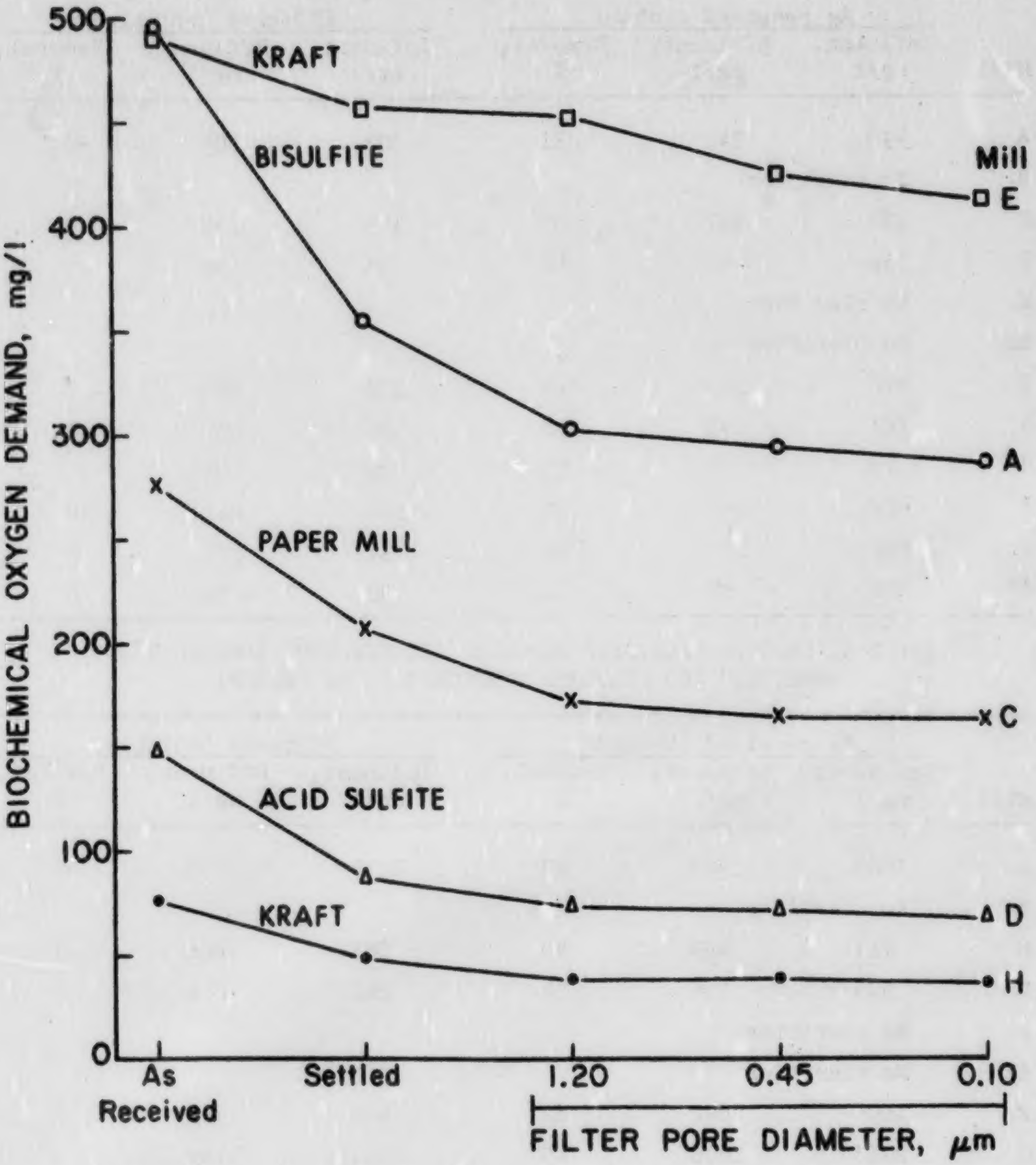


Figure 2. The separation of insoluble from soluble BOD_5 by filters of various pore sizes.

TABLE 5. BOD_5 IN CLARIFIER INFLUENT AND EFFLUENT SAMPLES ("AS RECEIVED" AND FILTERED THROUGH A 0.45 µm FILTER)

	As received (total)			Filtered (soluble)		
Mill	Influent, mg/l	Effluent, mg/l	Removal, %	Influent, mg/l	Effluent, mg/l	Removal, %
A	495	341	31	303	304	-0.3
B	No clarifier					
C	264	192	27	145	138	5
D	156	90	42	75	59	22
E	No clarifier					
EE	No clarifier					
F	378	322	15	179	200	-12
G	787	645	18	536	432	45
H	76	51	33	39	33	15
I	622	557	10	371	247	34
J	230	152	33	134	124	8
JJ	122	37	70	38	32	16

TABLE 6. COD IN CLARIFIER INFLUENT AND EFFLUENT SAMPLES ("AS RECEIVED" AND FILTERED THROUGH 0.45 µm FILTER)

	As received (total)			Filtered (soluble)		
Mill	Influent, mg/l	Effluent, mg/l	Removal, %	Influent, mg/l	Effluent, mg/l	Removal, %
A	1863	1328	29	1207	1236	-2
B	No clarifier					
C	712	429	40	283	286	-1
D	583	386	34	246	254	-3
E	No clarifier					
EE	No clarifier					
F	1695	642	62	408	399	2
G	2918	1606	45	1201	1149	4
H	272	188	31	108	98	9
I	2132	2013	6	1144	1104	4
J	715	433	40	351	284	19
JJ	691	126	82	88	84	5

the fact that both were collected within the same time period. This lack of continuity in the two samples could explain not only the lack of removal observed at times but could also be the reason that our studies showed the higher or lower removal values than did general mill experience.

TABLE 7. SUSPENDED SOLIDS IN CLARIFIER INFLUENT AND EFFLUENT SAMPLES REMOVED BY A 0.45 μm FILTER

Mill	Influent, mg/l	Effluent, mg/l	Removal, %
A	441	63	86
B	No clarifier		
C	1126	248	78
D	235	77	67
E	No clarifier		
EE	No clarifier		
F	1187	213	82
G	4165	1034	75
H	240	99	59
I	853	587	31
J	690	340	47
JJ	581	50	91

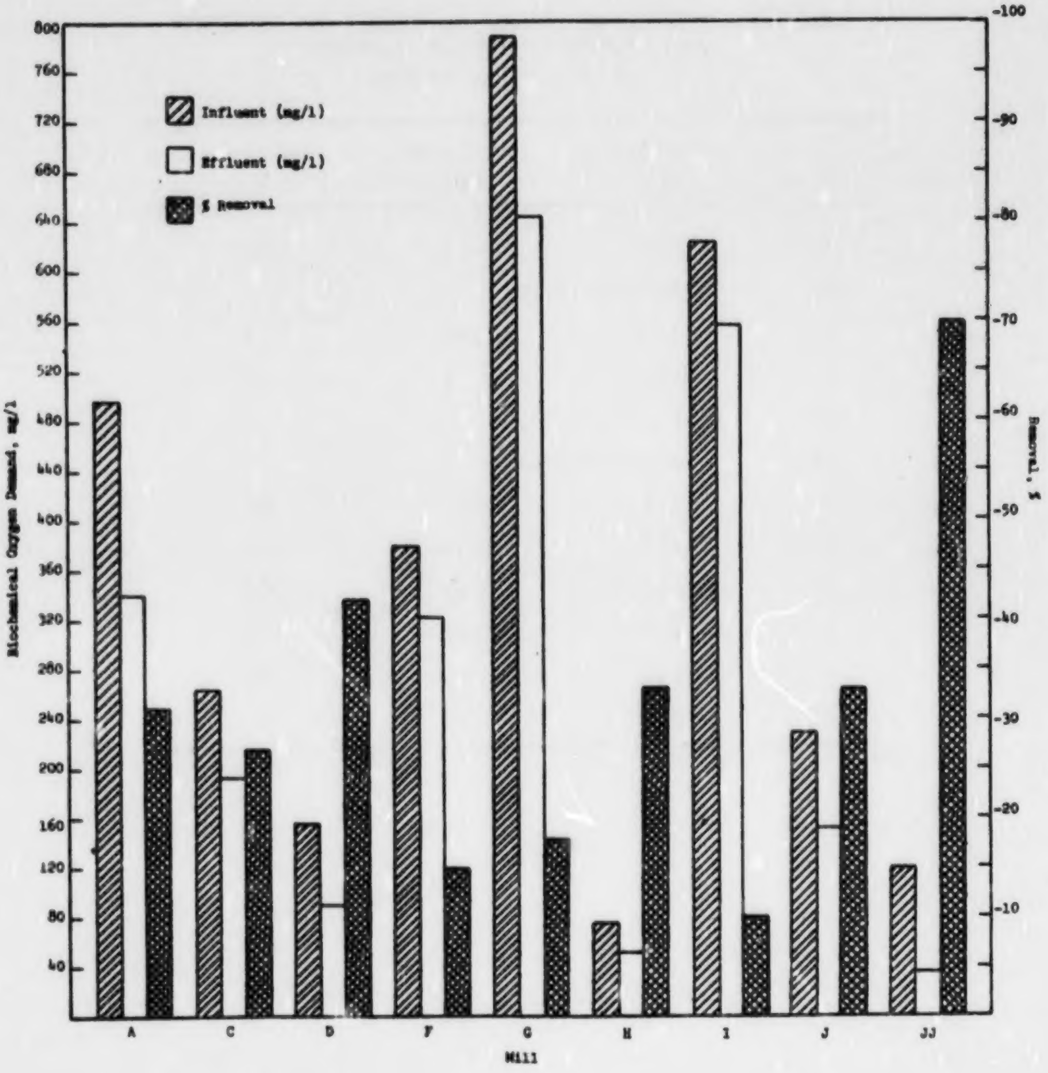


Figure 3. Total biochemical oxygen demand in clarifier influent and effluent samples.

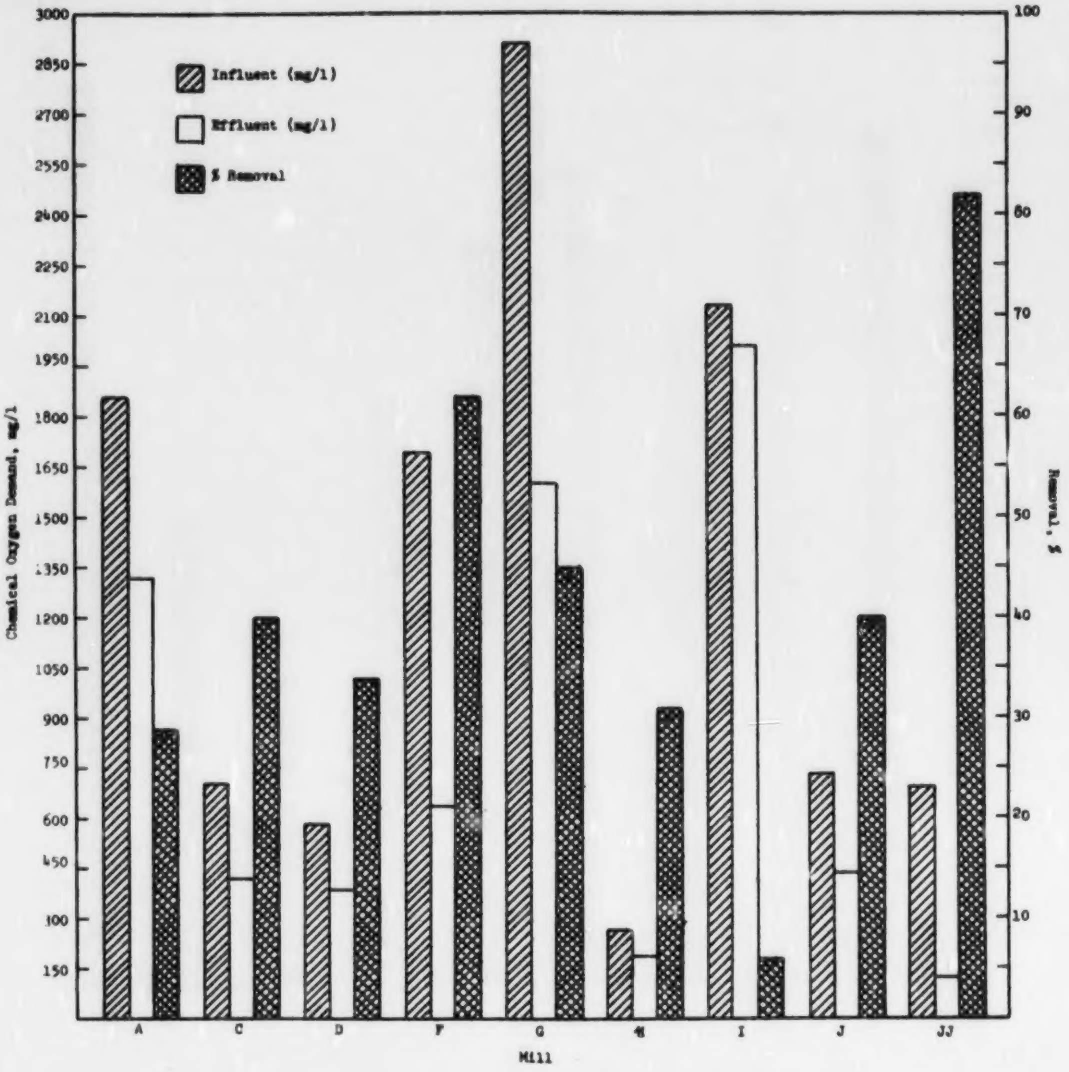


Figure 4. Total chemical oxygen demand in clarifier influent and effluent samples.

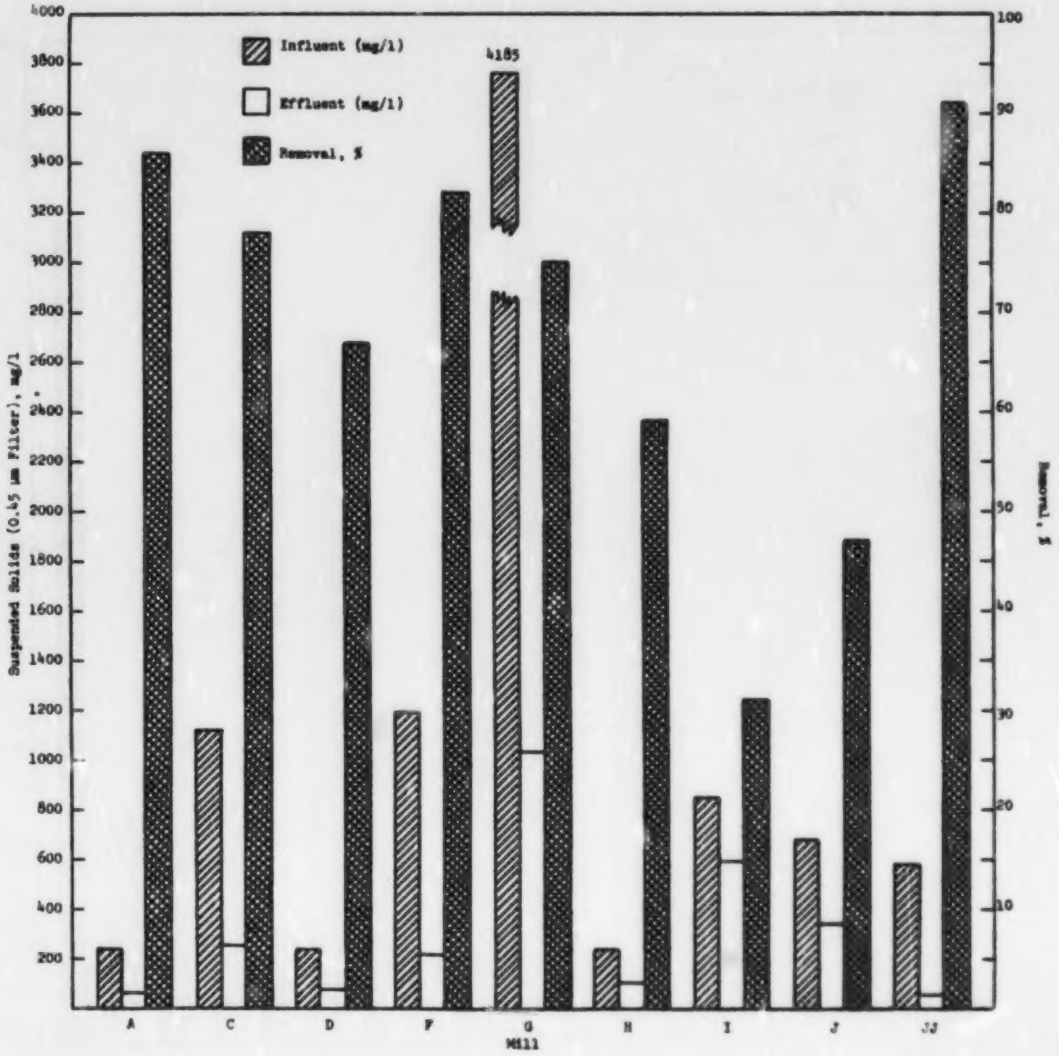


Figure 5. Suspended solids in clarifier influent and effluent collected on a 0.45-µm filter.

TABLE 8. THE VARIABILITY OF pH, BOD_5 AND COD IN CLARIFIER INFLUENT AND EFFLUENT SAMPLES FROM DIFFERENT SOURCES[a,b]

Influent			Effluent		
pH	BOD_5	COD	pH	BOD_5	COD
4.81	274	2268	6.88	268	552
8.28	884	3899	10.68	555	1548
10.42	482	1702	11.05	489	812
11.53	634	2498	9.88	777[c]	2202
10.18	836	3388	10.80	1104[c]	2478
7.35	476	1413	9.80	822[c]	2293
7.11	168	411	10.78	258[c]	869

[a] These values are from all of the samples (54 sets) where pH differences and/or negative "removal" was noted.

[b] Influent and effluent samples were taken during the same time period.

[c] Prolonged holding time probably explained the apparent negative removal.

SECTION V

LABORATORY STUDY OF PROCESSES FOR HIGHER LEVELS OF SOLUBLE BOD$_5$ REMOVAL

We approached the problems of improving pulp and paper mill liquid waste treatment by two differing routes. A first route studied possibilities for improving the methods for conventional, out-plant primary clarification treatment of the total mill discharge. The second, a more innovative route, was directed to the principle of separation of flows, particularly spills of strong process water, and was also directed to individual, high-efficiency treatments, preferably within the plant, for those flows detrimental to clarifier performance.

Various treatment methods, such as sedimentation, flotation, filtration, membrane separation (reverse osmosis, ultrafiltration), carbon adsorption, and ion exchange could be used. The results of some of these methods are described in this section.

New and relatively more expensive methods of processing would be feasible for only parts of the total flow in order to prevent buildup of solubles in streams, especially those being recycled. These fractions could be treated in-plant in small, highly efficient systems or, if the streams are not to be recycled, they could be treated before they are mixed with other process waters entering the total sewer system.

However, since many of the mills involved in this study were already using clarifiers or had plans to use them, the laboratory study was carefully planned to develop a better understanding of the conventional, out-plant clarification process.

SCREENING TESTS

Following the survey of mill discharges and clarifier efficiencies (Section IV), a study to optimize the removal of soluble BOD$_5$ from both total mill waste waters and individual streams was begun in the laboratory.

We preferred to evaluate clarification efficiency by some means other than the BOD$_5$ test because the 5-10 days time to run each test, depending upon the day of the week that the samples were prepared, made systematic laboratory studies very difficult. Also, we wanted a procedure based on small sample volume.

TEST TUBE TRIALS

We had developed in our laboratory a simple test tube flocculation test using a 15-ml sample in an 18 x 150 mm test tube mounted on a 12-inch diameter, vertically oriented, platform rotating at 3 rpm (unpublished). The slow transfer of fluid from one end of the tube to the other produced a floc form and supernatant clarity that correlated well with jar tests with the same sample/flocculant combination. This simple, small-volume system was used in the early part of the work for screening the incoming samples.

JAR TESTS

At the same time, jar tests were carried out on the same waste material using a Phipps and Bird laboratory flocculator. Various flocculating agents, alone or in combination, were added under carefully standardized conditions of chemical addition, rapid mixing, flocculation mixing, settling and sampling. Briefly, these can be described as:

1. The treatment of 1.0 or 1.5 liters of waste in 3-liter jars;
2. The addition of the primary flocculant, followed by one minute of mixing at 100 rpm;
3. If a second agent (e.g., polymer, silica, activated carbon, etc.) was added, it was followed by a second rapid mix of one-half minute at 100 rpm;
4. The paddle speed was reduced to 20 rpm for 20 minutes to provide time for flocculation. The flocculation step was done after the final addition of chemical, no matter how many additives were involved;
5. At the end of the flocculation period, the jar was removed from the unit and the sample allowed to settle for one hour;
6. Samples were withdrawn into 250-ml bottles under slight vacuum, with the tip of the sample tube one-half inch under the surface of the liquid in the jar;
7. An untreated jar of the waste was carried through the entire test from rapid mix to sampling. All "removal" data are based on the comparison of the analyses of the control sample with the treated samples.

All samples were stored at 4°C (40°F) prior to analysis.

ORGANIC CARBON ANALYSIS

Use of a Beckman Process Carbonaceous Analyzer permitted relatively rapid (15 samples per day), small-volume analysis of solutions for total organic carbon (TOC). The test tube trials, after the floc was removed with the 0.45-µm filter, provided sufficient sample for the determination of soluble organic carbon. The use of larger test tubes (25 x 250 mm) and additional sample volume on the same flocculator table, or jar tests directly, allowed determination of both total and soluble BOD_5 and TOC, and soluble organic carbon (OC) on the same sample.

We found little correlation between the reduction of soluble organic carbon and the reduction of soluble BOD_5 for a series of flocculation studies (Table 9). We also found no relationship of COD to BOD_5 during the mill survey; these results are probably due to the high ratio of nonbiodegradable to biodegradable carbon in these waste streams. Total and soluble organic carbon and BOD_5 components removed during flocculation would be both degradable and nondegradable substances, with the percentage removal of degradable being overshadowed by nondegradables. While the polymers did have both biochemical and chemical oxygen demands (Table 10), the amounts added to the solutions were so small (1 to 10 mg/liter) that they did not contribute significantly to COD or BOD_5. The addition of the polymer at the 10 mg/liter level would add less than 2 percent COD and 1 percent BOD_5 to most samples if all of the polymer remained in solution and none was removed by flocculation and/or filtration.

TABLE 9. SCREENING TRIALS OF FLOCCULANTS AND POLYMERS BY ANALYSIS OF SOLUBLE ORGANIC CARBON AND SOLUBLE BOD_5

Flocculant		Polymer	Reduction[a], %	
Type	mg/l	(0.5 mg/l)	Soluble OC	Soluble BOD_5
Alum	200	None	18.2	-9.7
Alum	200	Nalco 607	34.3	-20.9
	250	Nalco 627	26.5	8.1
	250	Nalco 634	15.7	5.4
	250	Nalco 73C32	6.0	0
$FeCl_3$	100[b]	None	20.7	20.3
	150	None	17.4	-20.5
	200	None	25.4	21.2
	200	Nalco 607	21.3	16.8
	200	Nalco 609	23.1	20.7
	200	Nalco 627	-7.4	15.7
	250	None	20.5	19.7
Lime	25	None	1.8	-1.9
	25	Nalco 634	-6.2	8.4
	25	Nalco 73C32	2.3	0

[a] Values on "as received" samples:

Soluble OC = 125-425 mg/l.
Soluble BOD_5 = 100-200 mg/l.

[b] As Fe^{3+}.

TABLE 10. COD AND BOD_5 OF VARIOUS POLYMERS USED AS FLOCCULATION AIDS[a]

Manufacturer	Soluble COD, mg/l	Soluble BOD_5, mg/l
Nalco		
607	231	0
609	740	14
634	333	0
73C32	402	0
Dow		
PAA	1544	214
Tydex 12	1665	0
Hercules		
Hercofloc 812.3	--	66

[a] Polymer concentration 1 g/l.

PHENOL SULFURIC ACID TEST

The phenol-sulfuric acid test (7) is a rapid method for the estimation of carbohydrates, including virtually all classes of sugars, sugar derivatives, oligo- and polysaccharides, ketoses, aldoses and aldehydes. This method has been used for several years in these laboratories for monitoring gel chromatographic columns and for the study of aldehydes in solution, both carbohydrates and noncarbohydrates (8).

Although the method appeared to be useful for measuring the removal of soluble BOD_5 during trials in the test tubes (Table 11), it did not give reproducible results in the jar tests; therefore, it was not useful as a replacement for the BOD_5 test (Table 12).

ZETA POTENTIAL

"If the zeta potential of the colloid is lowered below a critical value, the colloids tend to coalesce, resulting in coagulation" (9). Many of the "soluble" BOD_5 components in the waste stream are colloids, medium and low molecular weight organics, and in some cases simpler carbonaceous compounds, which should be amenable to colloidal coagulation and coprecipitation (10). Zeta potential changes and final values were compared with the removal of COD and BOD_5 components by flocculation (Table 13). No correlation could be drawn between the zeta potential and the reduction of either COD or BOD_5 for the waste stream after flocculation and filtration. There was, however, the expected correlation of near zero zeta potentials with good floc formation and supernatant clarity.

TABLE 11. COMPARISON OF PHENOL SULFURIC ACID TEST WITH BOD_5 TEST TO EVALUATE FLOCCULANTS IN TEST TUBE TESTS

Flocculant		Polymer	Reduction,[a] %	
Type	mg/l	(1 mg/l)	Soluble glucose equivalent	Soluble BOD_5
$FeCl_3$	50[b]	None	28.9	22.8
	100	None	45.6	32.1
	150	None	50.0	36.2
	200	None	46.7	33.9
Lime	250	None	17.7	5.0
	300	None	6.3	18.4
	300	Nalco 609	25.6	16.4
	300	Nalco 627	40.5	12.9
	300	Nalco 634	40.5	25.9
	300	Nalco 73C32	20.0	12.9
	300	Dow PAA	39.1	23.2
	300	Dow Tydex 12	32.6	31.7
	400	None	28.1	7.1

[a] Values "as received":

Soluble glucose equivalent = 216 mg/l.
Soluble BOD_5 = 200 mg/l.

[b] As Fe^{3+}.

As the study progressed we found little relation of the visual clarity of the supernatant or the rate of floc settling with the reduction of BOD_5. A finely divided floc seemed to result in the greatest reduction in soluble BOD_5 after filtration with the 0.45-μm filter, whether or not the floc had settled.

JAR TESTS FOR OPTIMIZING BOD_5 REMOVAL BY CLARIFICATION

General

Following the lack of success in developing a rapid screening test to correlate flocculation with the removal of soluble BOD_5, a number of jar tests were made with several mill effluents. We used the standard BOD_5 analysis to test these flocculants. While this resulted in a rather delayed evaluation, it could be used for: (1) a study of many flocculating agents and variables or (2) careful consideration and selection of both flocculants and process variables, with BOD_5 determinations on either (a) all samples or (b) selected samples from each series. With frequent reevaluation of the procedure as BOD_5 results became available, the (2b) scheme was selected for the majority of the jar tests.

TABLE 12. COMPARISON OF PHENOL SULFURIC ACID TEST WITH BOD_5 TEST TO EVALUATE FLOCCULANTS IN JAR TESTS

Flocculant			Reduction[a], %		
Manufacturer	mg/l	pH	Soluble glucose equivalent	Soluble BOD_5	Soluble COD
Nalco					
607	6.0	7.5	-1.5	2.6	-1.8
609	6.0	3.0	12.0	11.3	10.2
	6.0	7.5	11.5	6.8	7.2
	10.0	7.5	16.5	9.8	7.2
627	6.0	3.0	4.5	8.4	5.9
634	6.0	7.5	7.3	6.8	2.7
	10.0	7.5	15.3	10.0	16.6
73C32	6.0	7.5	7.3	-2.1	1.8
	10.0	7.5	11.5	23.8	5.4
Dow					
PAA	6.0	7.5	15.3	2.1	8.6
	10.0	7.5	15.3	12.8	9.3
	20.0	5.0	10.8	-1.7	4.2
Tydex 12	6.0	3.0	3.2	4.6	1.3
	6.0	5.0	-1.2	-24.8	3.3
	6.0	7.5	7.3	8.1	3.8
	10.0	7.5	14.2	5.1	6.8

[a] Values "as received":

Soluble glucose equivalent = 250 mg/l.
Soluble COD = 550 mg/l.
Soluble BOD_5 = 220 mg/l.

TABLE 13. A COMPARISON OF ZETA POTENTIAL, SOLUBLE COD AND BOD_5, AND FLOC FORM IN JAR TESTS OF FLOCCULANTS

Flocculant				Zeta potential,	Reduction[b], %		
Type	mg/l	Effluent[a]	pH	mv	Soluble COD	Soluble BOD_5	Floc[c] form
Alum	200	A	--	-9.3	2.1	0.0	--
	395	B	--	0	17.3	-1.5	4+
	632	B	--	0	12.2	3.6	4+
Fe^{3+}	50	C	--	0 to -24.5	16.8	5.3	--
	75	C	--	0	23.2	11.9	--
	84	B	3.0	0	30.5	21.9	4+
	84	B	5.0	-17.8	33.3	17.2	3+
	200	A	3.0	0	45.3	51.0	--
Lime	200	A	11.6	-20.2	4.0	5.8	--

[a] A = special sample of beaten sulfite pulp.
B = total mill effluent (Mill F).
C = digester room effluent (Mill F).

[b] Values for "as recieved":

A — soluble COD = 462 mg/l.
soluble BOD_5 = 128 mg/l.

B — soluble COD = 453 mg/l.
soluble BOD_5 = 190 mg/l.

C — soluble COD = 1284 mg/l.
soluble BOD_5 = 585 mg/l.

[c] Floc form — 0 = supernatant clarity equal to untreated control.
5+ = clear supernatant without suspended solids.

To reduce the problem involved in setting up sampling schedules, sample transportation and storage, it was further decided to select mills by two criteria: (1) their proximity to our Appleton laboratories and (2) those having high soluble BOD_5 values in the initial survey. Others could be added, as time permitted, to allow studies of special effluents, of effluents with lower soluble BOD_5, or of effluents from more distant mills.

TOTAL MILL EFFLUENTS WITH PRIMARY FLOCCULANTS

Tables 14, 15 and 16 summarize the large volumes of data gathered from jar tests with effluents from Mills A, D, and F, which are using conventional clarifiers or flotation systems. These data can be summarized as follows:

1. Ferric chloride in the range of 75-150 mg/l Fe^{3+} was the best flocculating agent for these waste streams. The optimum pH was dependent upon the particular stream being processed and the concentration of the iron salt added.
2. Lime, at higher concentrations (200-500 mg/l) also removed soluble BOD_5 (21-40 percent).
3. Alum did not remove more than 17 percent of the soluble BOD_5, although there was evidence that, with some of the waste streams, careful pH control and optimized alum concentrations could result in the removal of substantial quantities of soluble BOD_5.
4. The polymers plus bentonite or Celite to provide high surface area did not appear any more effective than the cheaper iron salts.
5. Some trials had shown that considerable amounts (22 percent) of soluble BOD_5 could be removed from the clarifier effluents with ferric chloride or lime (Table 14).
6. When the concentration of the flocculating agent and the pH are carefully controlled, from 25 to 50 percent of the soluble BOD_5 would probably be removed from the clarifier influents.
7. In recent similar studies in Finland (11), fly ash obtained from the burning of calcium-base spent liquor was used as a flocculating agent, it was used to raise the pH during alum treatment, and it was used as a sludge conditioner. Reductions of 50 percent for BOD_5 and 70 percent for COD are reported in the treatment of kraft effluents. The authors also report that the sludge is easier to handle.

ADDITION OF ACTIVATED CARBON

Studying pilot-scale columns of activated carbon processing a chemimechanical (CM) pulping waste, we found that 83-90 percent of the total BOD_5 was removed (12). We have no information, however, on the degree of soluble BOD_5 removed by adsorption on activated carbon. Therefore, we used jar tests to measure the reduction in soluble BOD_5 by powdered (300 mesh) activated carbon, with and without the addition of cationic polyelectrolytes, for the treatment of the total mill effluent (Table 17) and CM sewer discharge from Mill F (Table 18).

Soluble BOD_5 could be reduced by 32 percent in the total mill effluent and 17 percent in the CM streams. The variability of the results for the various levels of activated carbon was quite high. This was most likely due to changing conditions in the mill — high hourly variations in the flow and concentration of substances in these streams — rather than to differences in the effects of the activated carbon and polymers.

TABLE 14. JAR TESTS OF PRIMARY FLOCCULANTS WITH MILL A AND MILL D INFLUENTS AND EFFLUENTS[a]

Flocculant		Final	Mill A influent No additive COD = 1200 mg/l BOD$_5$ = 238 mg/l		Mill A influent 2 mg/l Gendriv 162 COD = 1178 mg/l BOD$_5$ = 228 mg/l		Mill A effluent 2 mg/l Gendriv 162 COD = 1126 mg/l BOD$_5$ = 238 mg/l		Mill D influent No additive COD = 843 mg/l BOD$_5$ = 292 mg/l	
			Reduction, %		Reduction, %		Reduction, %		Reduction, %	
Type	mg/l	pH	COD	BOD$_5$	COD	BOD$_5$	COD	BOD$_5$	COD	BOD$_5$
None	pH study	3.6	--	--	0	0	0.4	0	3.3	--
		3.8	--	--	0	0	0.9	0	0	--
		4.0	--	--	0	3.9	2.1	0	2.0	1.4
		4.2	--	--	0.1	0	0.9	0	0	-1.4
		4.4	--	--	0	0	0.9	0	1.1	1.4
		4.6	--	--	0	0	0.4	0	3.6	2.4
Fe^{3+}	70[b]	3.6	31.8	14.3	23.6	21.0	22.9	22.3	22.4	--
	70	3.8	31.6	13.4	26.4	25.5	23.4	21.8	21.9	--
	70	4.0	23.8	10.1	27.5	13.2	24.1	10.9	22.2	-1.4
	70	4.2	23.3	11.3	27.2	3.7	26.8	12.7	21.7	14.0
	70	4.4	22.9	11.8	26.8	19.3	24.2	15.9	21.9	21.2
	70	4.6	23.3	8.4	26.4	13.9	6.5	20.9	23.2	13.4
	70	10.0	7.8	17.2	--	--	23.0	13.2	25.1	
Lime	50	8.2	--	--	1.8	--	0.3	5.4		
	50	8.6	--	--	--	--	--	--	2.8	4.4
	50	8.9	--	--	--	--	--	--	--	--
	100	9.2	2.8	13.4	1.3	--	0.3	1.8	--	--
	100	10.0	--	--	--	--	--	--	3.6	-1.4
	200	9.9	--	--	--	--	4.3	5.4	--	--
	200	10.1	4.9	11.8	4.8	--	--	--	9.0	-2.7
	200	11.2	--	--	--	--	--	--	--	--
	300	10.8	--	--	--	--	8.2	2.7	--	--
	400	11.2	22.0	15.5	22.4	--	19.2	3.6	--	--
	400	11.7	--	--	--	--	--	--	16.7	-4.5
	500	11.5	24.6	18.1	25.8	--	24.6	1.4	--	
	500	11.8	--	--	--	--	--	--	18.0	15.4

---

[a] Soluble COD and BOD$_5$ were measured.

[b] As $FeCl_3$.

TABLE 15. JAR TESTS OF PRIMARY FLOCCULANTS WITH MILL F TOTAL CLARIFIER INFLUENT[a]

Flocculant		Final	Sample 8/13 COD = 508 mg/l BOD_5 = 223 mg/l		Sample 8/21 COD = 209 mg/l BOD_5 = 102 mg/l		Sample 9/10 COD = 440 mg/l BOD_5 = 194 mg/l	
			Reduction, %		Reduction, %		Reduction, %	
Type	mg/l	pH	COD	BOD_5	COD	BOD_5	COD	BOD_5
Lime	50	8.8	-7.2	-10.2	-3.8	0	--	--
	100	9.2	0	-10.2	-1.9	0	--	--
	200	10.6	7.2	-1.6	10.0	21.4	--	--
	800	11.4	11.8	3.7	14.8	18.4	--	--
	400	11.6	12.9	15.5	17.1	36.7	--	--
	500	11.7	--	--	20.0	40.0	--	--
Bentonite	50	--	5.1	1.4	--	--	--	--
	100	--	7.6	1.0	--	--	--	--
	150	--	6.5	-3.6	--	--	--	--
	200	--	7.6	-1.4	--	--	--	--
Fe^{3+}	12.5	6.8	--	--	5.4	1.4	--	--
(as $FeCl_3$)	25	6.5	--	--	8.9	1.4	--	--
	28[b]	2.7	--	--	--	--	12.9	7.5
	50	5.7	--	--	19.8	7.2	--	--
	70[b]	5.2	--	--	--	--	31.3	5.2
	70[b]	4.6	--	--	--	--	35.8	24.0
	70[b]	4.1	--	--	--	--	34.8	22.4
	70[b]	8.6	--	--	--	--	33.7	8.8
	70[b]	3.5	--	--	--	--	28.0	6.2
	84[b]	5.1	--	--	--	--	33.3	12.2
	84[b]	4.2	--	--	--	--	33.7	18.8
	84[b]	3.2	--	--	--	--	30.5	21.9
	100	3.3	--	--	15.8	8.7	--	--
	112[b]	6.0	--	--	--	--	32.4	17.5
	112[b]	3.8	--	--	--	--	30.7	11.3
	150	2.9	--	--	13.9	10.1	--	--
	200	2.7	--	--	15.8	18.8	--	--
Alum	25	--	--	--	9.0	-1.0	--	--
	50	--	--	--	4.3	4.9	--	--
	100	--	--	--	3.8	3.9	--	--
	150	--	--	--	5.2	2.0	--	--
	158[b]	3.5	--	--	--	--	8.2	3.0
	200	--	--	--	10.0	2.0	--	--
	250	--	--	--	10.0	2.0	--	--
	385[b]	8.9	--	--	--	--	8.7	-5.2
	385[b]	6.8	--	--	--	--	19.2	-24.2
	385[b]	6.2	--	--	--	--	21.9	12.0
	385[b]	5.3	--	--	--	--	21.9	-18.3
	385[b]	4.6	--	--	--	--	23.9	16.7
	385[b]	4.3	--	--	--	--	19.2	11.4
	385[b]	3.9	--	--	--	--	11.9	7.3
	632[b]	10.6	--	--	--	--	12.2	3.6
	632[b]	6.9	--	--	--	--	17.8	-2.1

[a] Soluble COD and BOD_5 were measured.

[b] Added on molar basis of Fe^{3+} and Al^{3+} (0.5, 1.25, 2.0 millimolar).

TABLE 16. JAR TESTS OF POLYMERS AND ADDITIVES WITH MILL F TOTAL CLARIFIER INFLUENT[a]

					Sample 7/31 COD = 552 mg/l BOD$_5$ = 234 mg/l		Sample 8/13 COD = 508 mg/l BOD$_5$ = 223 mg/l	
Flocculant		Additive[b]		Final	Reduction, %		Reduction, %	
Manufacturer	mg/l	Type	mg/l	pH	COD	BOD$_5$	COD	BOD$_5$
Nalco								
607	1.0	Bentonite	200	--	--	--	8.2	11.9
607	1.0	A/C	200		--	--	7.0	-4.6
607	6.0	None	--	7.5	-1.8	2.6	--	--
609	1.0	Bentonite	200	--	--	--	9.4	3.2
609	1.0	A/C	200	--	--	--	8.2	18.7
609	6.0	None	--	7.5	6.8	7.2	--	--
609	6.0	None	--	3.0	10.2	11.3	--	--
609	10.0	None	--	7.5	7.2	9.8	--	--
627	1.0	Bentonite	200	--	--	--	9.2	1.8
627	1.0	A/C	200	--	--	--	9.6	16.9
627	6.0	None	--	3.0	5.9	8.4	--	--
634	1.0	Bentonite	200	--	--	--	8.0	-1.4
634	1.0	A/C	200	--	--	--	5.1	1.4
634	6.0	None	--	7.5	2.7	6.8	--	--
634	10.0	None	--	7.5	10.0	16.6	6.7	23.8
73C32	1.0	Bentonite	200	--	--	--	7.4	9.1
73C32	1.0	A/C	200	--	--	--	8.0	19.6
73C32	6.0	None	--	7.5	1.8	-2.1	--	--
73C32	10.0	None	--	7.5	5.4	23.8	6.1	29.4
73C32	10.0	Celite	200	7.5	--		3.0	21.2
Dow								
Tydex 12	1.0	Bentonite	200	--	--	--	12.4	-1.4
Tydex 12	1.0	A/C	200	--	--	--	9.0	20.5
Tydex 12	6.0	None	--	7.5	3.8	8.1	--	--
Tydex 12	6.0	None	--	5.0	3.3	-24.8	--	--
Tydex 12	6.0	None	--	3.0	1.3	4.6	--	--
Tydex 12	10.0	None	--	7.5	6.8	5.1	--	--
PAA	1.0	Bentonite	200	--	--	--	14.7	-4.5
PAA	1.0	A/C	200	--	--	--	8.6	-11.4
PAA	6.0	None	--	7.5	8.6	2.1	--	--
PAA	10.0	None	--	7.5	9.3	12.8	6.3	21.8
PAA	10.0	Celite	200	--	--	--	7.4	14.2
PAA	20.0	None	--	5.0	4.2	-1.7	--	--

[a] Soluble COD and BOD$_5$ were measured.

[b] A/C = activated carbon (Filtrasorb 300, powdered).

TABLE 17. JAR TESTS OF THE EFFECT OF ACTIVATED CARBON AND VARIOUS ADDITIVES ON SOLUBLE COD AND BOD_5 IN MILL F CLARIFIER INFLUENT

Activated carbon		Additives		Final pH	Sample 8/13 COD = 508 mg/l BOD_5 = 223 mg/l Reduction, %		Sample 8/21 COD = 209 mg/l BOD_5 = 102 mg/l Reduction, %		Sample 9/10 COD = 426 mg/l BOD_5 = 196 mg/l Reduction, %	
Type[a]	mg/l	Type	mg/l		COD	BOD_5	COD	BOD_5	COD	BOD_5
(1)	50	None	--	7.4	6.1	19.2	4.1	3.4	--	--
	100	None	--	7.5	5.7	8.7	6.9	--	--	--
	150	None	--	7.5	5.9	12.3	--	--	--	--
	200	None	--	7.4	5.7	-5.5	13.4	11.5	3.5	2.0
	200	Nalco 73C32	1.0	7.5	8.0	19.6	--	--	6.3	23.5
	200	Dow Tydex	1.0	7.4	9.0	20.5	--	--	5.2	6.1
	200	Cellulose	500	--	--	--	--	--	5.2	12.2
	200	Nalco 609	1.0	7.9	8.2	18.7	--	--	--	--
	200	Nalco 627	1.0	7.9	9.6	16.9	--	--	--	--
	200	Nalco 634	1.0	7.8	5.1	1.4	--	--	--	--
	200	Dow PAA	1.0	7.9	8.6	—	--	--	--	--
(2)	50	None	--	--	--	--	14.7	17.0	--	--
	100	None	--	--	--	--	17.4	7.5	--	--
	200	None	--	--	--	--	11.9	27.4	--	--
	200	Nalco 73C32	1.0	--	--	--	--	--	16.4	12.2
	200	Dow Tydex	1.0	--	--	--	--	--	7.5	9.2
	200	Cellulose	500	--	--	--	--	--	8.0	11.2
	200	Cellulose	500	--	--	--	--	--	4.0	19.4
		+ Tydex	1.0	--	--	--	--	--	--	--
	200	Cellulose	500	--	--	--	--	--	5.2	14.3
		+ 73C32	1.0	--	--	--	--	--	--	--
	300	None	--	--	--	--	17.9	13.2	--	--
	400	None	--	--	--	--	17.9	32.1	--	--

[a] (1) Filtrasorb 300, powdered.
(2) Same alcohol and water washed (oven dried).

In all of the jar tests the samples were first screened through a 60-mesh stainless steel screen, the activated carbon (and polymers, if used) was added, and the sample was processed through the mixing and settling cycles.

No attempt was made to correlate the degree of soluble BOD_5 removal with the presence of fiber fines or other carbonaceous adsorbing materials.

Although the activated carbon-soluble BOD_5 complex could be readily filtered by a 0.45-µm filter, it did not settle in the jars with or without the use of polymer flocculants. Activated carbon, therefore, seems useful as an additive to the primary system for the reduction of BOD_5 if the carbon could be removed in either the primary or secondary system. Larger carbon particles might be easier to remove; however, they would have less surface area and, therefore, probably be less sorptive.

EFFECT OF THE CONCENTRATION OF THE EFFLUENT

If the total water use in the mill were reduced through recycling, the wastes would be more concentrated. In order to study the flocculation and soluble BOD_5 removal characteristics of such wastes we concentrated by reverse osmosis a sample of the total mill effluent (clarifier influent) from the Mosinee mill. We have been evaluating and developing uses for reverse osmosis (RO) in our laboratories since 1964 (13). This process can concentrate solutions and at the same time remove some of the soluble BOD_5.

TABLE 18. JAR TESTS OF THE EFFECT OF ACTIVATED CARBON AND ADDITIVES ON COD AND BOD_5 OF MILL F CHEMIMECHANICAL PULPING EFFLUENT[a]

Carbon,[b] mg/l	Additive		Reduction, %		Final pH
	Type	mg/l	COD	BOD_5	
50	None	--	2.5	15.9	7.4
100	None	--	3.4	--	7.5
125	None	--	5.9	11.6	7.6
150	None	--	4.5	5.2	7.7
200	None	--	5.2	12.0	7.5
200	Nalco 634	10.0	4.3	2.0	7.5
200	Nalco 73C32	10.0	5.9	13.1	7.5
200	Dow Tydex 12	10.0	10.0	9.0	7.5
200	Dow PAA	10.0	10.5	16.8	7.5
300	None	--	10.2	9.8	7.5
None	Nalco 634	10.0	-1.0	-1.5	7.4
None	Nalco 73C32	10.0	1.0	5.9	7.4
None	Dow PAA	10.0	-4.1	-5.1	7.6

[a] Soluble COD and BOD_5 were measured.

Initial values: Soluble COD = 1105 mg/l
Soluble BOD_5 = 490 mg/l.

[b] Activated carbon — Filtrasorb 300, powdered, alcohol/water washed, oven dried.

Reverse osmosis was used to make a fourfold v/v concentrate of the total mill effluent. This solution was diluted with the permeate (fluid passing through the RO membrane during the concentration process) to prepare 3:1, 2:1, and 1:1 concentrations. Jar tests were made with all concentrations, and the samples were analyzed for suspended solids, total and soluble BOD_5, and color before and after treatment with ferric chloride-polymer and alum-polymer combinations (Figure 6).

These data indicate that treatment with ferric chloride at 100 mg Fe^{3+} per liter and Hercofloc 812.3 at 0.75 mg per liter could produce an acceptable effluent for discharge, in terms of suspended solids and BOD_5, up to concentration of approximately 3:1 and reduce both hydraulic and gravimetric loads.

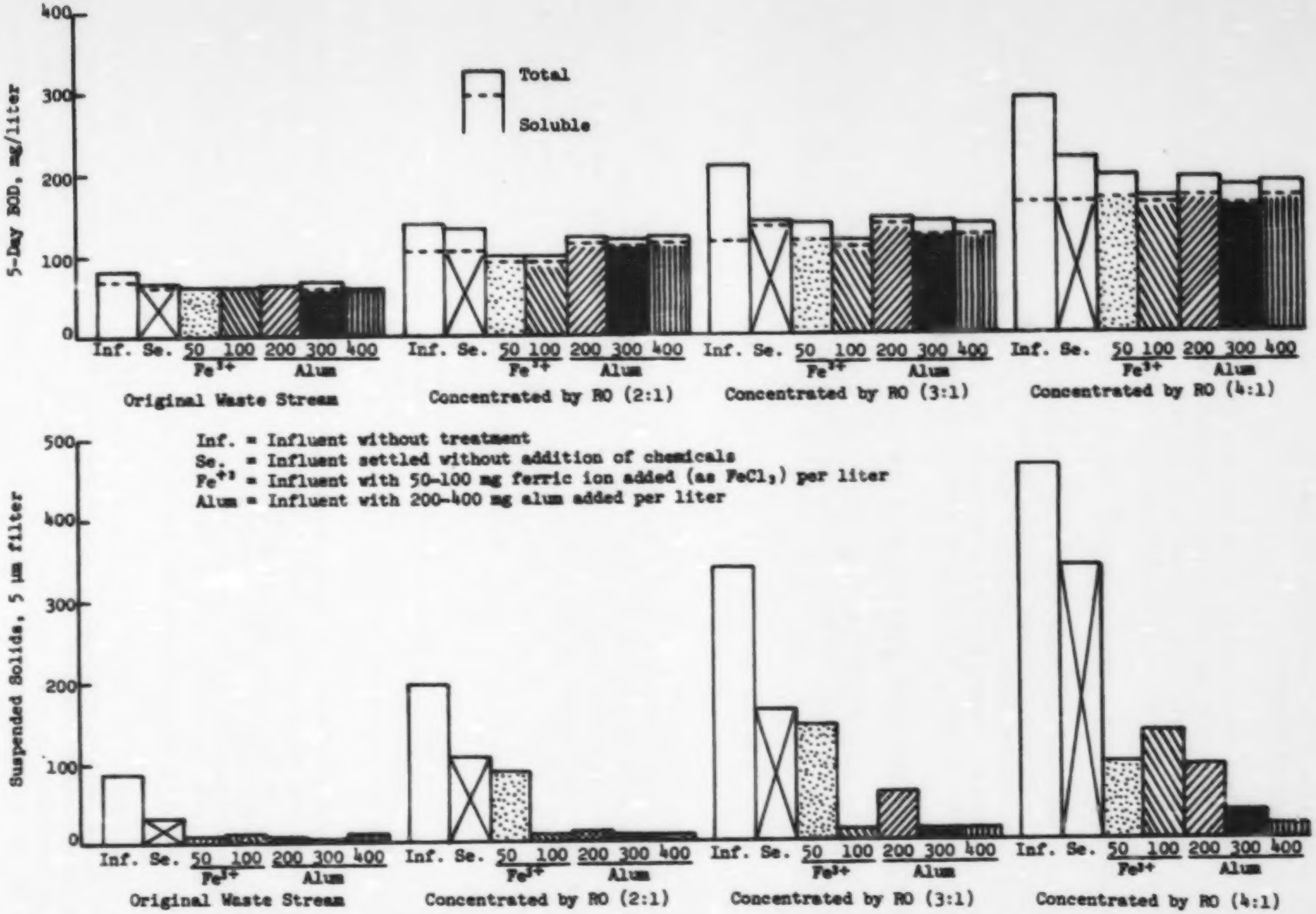


Figure 6. Suspended solids and BOD$_5$ in various concentrations of influents treated with Fe^{3+} or alum.

With effluents more concentrated than 3:1, flocculating agents did not produce adequate effluents.

While this was a rough study and practical means of processing were not worked out — we did not study spill control, the effect of spills on water reuse within the mill, or economics — it certainly indicates that wastes can be successfully treated at higher concentrations.

JAR TESTS ON WASTE STREAMS PRIOR TO PILOT SCALE TRIALS

Mosinee Paper Company of Mosinee, Wisconsin and the Combined Locks mill of Appleton Papers Division of NCR, Combined Locks, Wisconsin were selected for the two pilot-scale clarifier trials. Jar tests were made on the total mill effluents. These preliminary tests were followed periodically by other jar tests while the field trials were in progress.

Tests on Mosinee Paper Company Effluent

Samples from these jar tests were, in some cases, analyzed completely for suspended solids, total and soluble BOD_5, organic carbon, COD and color (Tables 19 and 20) in order to measure the removals that might be attained under different conditions of treatment. Others were merely used to establish flocculating characteristics (Table 21) and/or sludge volumes that would develop with the addition of the chemical combinations.

In the early trials we established that alum at 200-300 mg/l and ferric chloride at 100 mg/l Fe^{3+} could be used in jar tests to remove BOD_5 — 35-55 percent (total) and 12-25 percent (soluble) — from the wastes. The addition of 0.75 mg/l Hercofloc 812.3 appeared to provide additional removal of soluble BOD_5: removal increased from 13 to 35 percent when Hercofloc was added with 100 mg/l alum, and from 12 to 28 percent with 200 mg/l alum (Table 19). The use of the Hercofloc polymer alone at 0.75 and 1.5 mg/l markedly increased the removal of soluble BOD_5: we found 14 and 21 percent removal, respectively.

Lime as a primary flocculating agent and activated silica as an additive (Table 20) appeared to be relatively effective (4-16 percent) in the removal of soluble BOD_5 from the Mosinee mill effluent.

Of great interest in these studies was the high removal of COD, color, and total and soluble BOD_5 that could be achieved with ferric chloride and alum from the clarifier effluent from this mill (Table 22). Twenty-five to forty percent removal of the soluble BOD_5 components was obtained with these primary flocculants added to either the north or south clarifier effluents. Lime and "additional" Hercofloc 812.3 did not enhance the removal of the "solubles" but did increase the removal of total BOD_5, COD and color.

Adjustment of the pH from the initial 11, or higher, to 8 with sulfuric acid prior to the addition of the chemicals, markedly increased the amount of suspended solids removed. This only slightly affected the amount of soluble BOD_5 remaining in solution (Table 23). The ferric ion was equally effective as the chloride or sulfate salt when they were used at the same concentration

TABLE 19. JAR TESTS OF THE EFFECT OF FLOCCULANTS ON BOD_5, COD, ORGANIC CARBON, AND COLOR IN MOSINEE CLARIFIER INFLUENT[a]

			% Reduction in				
Flocculant		Final	Total		Soluble[b]		Total
Type	mg/l	pH	BOD_5	COD	OC	BOD_5	color[c]
$FeCl_3$	50[d]	6.4	51	71	31	13	52
	100	6.0	37	70	44	25	43
	150	5.0	58	76	47	24	89
Alum	100	7.2	49	60	14	13	24
	200	7.0	56	68	24	12	43
	300	6.8	56	73	31	12	47
Lime	200	11.1	22	52	-13	-16	15
	300	11.6	39	68	-1	-14	58
	500	12.0	41	71	1	-9	11
Hercofloc 812.3	0.75	8.4	18	8	3	14	0
	1.5	8.2	19	11	6	21	15
Hercofloc 812.3 at 0.75 mg/l was added after 1 min mixing with the following primary flocculant:							
$FeCl_3$	10	7.0	No floc formation				
	25	6.8	No floc formation				
	50	6.4	56	72	30	30	47
Alum	50	7.4	No floc formation				
	100	7.2	54	76	14	35	18
	200	7.0	52	71	21	28	32

---

[a] Initial control values for sample taken 11/21/74:

Total COD = 711 mg/l
BOD_5 = 215 mg/l
Color = 109 units.
Soluble OC = 87 mg/l
BOD_5 = 122 mg/l

[b] Filtered through a 0.45 μm Metricel filter.

[c] Co-Pt units at 465 nm (NCASI Method).

[d] As Fe^{3+}.

TABLE 20. JAR TESTS OF $FeCl_3$, ALUM, AND ADDITIVES AS FLOCCULANTS FOR MOSINEE CLARIFIER INFLUENT[a]

Flocculant			Final pH	Reduction, %				
				Total		Soluble		
Primary, mg/l	Polymer,[b]	mg/l		BOD_5	COD	OC	BOD_5	Color
Analytical grade primary chemicals:								
$FeCl_3$ 50[c]	--	--	5.8	38	56	49	29	88
	Herc.	0.75	5.8	37	57	51	27	89
		1.5	5.8	38	58	51	27	90
Alum 50	--	--	7.4	11	-0.7	20	9	39
	Herc.	0.75	7.5	10	-0.7	21	15	47
		1.5	7.7	6	0.7	14	10	45
	Act.Si	10	7.7	5	4	24	4	40
100	--	--	7.1	13	3	34	5	69
	Herc.	0.75	6.8	15	16	33	8	69
		1.5	7.1	10	3	34	16	72
	Act.Si	10	7.4	11	4	29	12	53
200	--	--	7.4	23	54	42	8	86
	Herc.	0.75	7.2	23	54	40	4	88
		1.5	7.0	21	47	39	4	87
	Act.Si	10	6.9	23	57	39	4	84
Commercial grade primary chemicals:								
$FeCl_3$ 50[c]	Herc.	0.75	5.5	32	50	--	28	--
Alum 100	Herc.	0.75	6.5	20	9	--	13	--

---

[a] Initial values (for untreated influent control) for sample taken 12/12/74:

Total COD = 711 mg/l
BOD_5 = 215 mg/l
Color = 109 Pt-Co units
Soluble OC = 87 mg/l
BOD_5 = 122 mg/l.

[b] Herc., Hercofloc 812.3; Act.Sci., activated silica.

[c] As Fe^{3+}.

of Fe^{3+} and when the pH of the influent was not above 9.0 (Figure 7). Sludge volumes, determined with separate jar tests and the Imhoff cone, were also markedly reduced by the addition of the Hercofloc 812.3 (Table 24) and for this reason it was included in all but one of the studies at this mill.

TABLE 21. JAR TESTS OF THE EFFECTS OF PRIMARY FLOCCULANTS AND POLYMERS ON pH AND CLARITY OF MOSINEE CLARIFIER INFLUENTS

Flocculant				Influent samples					
				1/16/75		3/5/75		3/11/75	
Primary, mg/l		Polymer, mg/l		pH	Clarity[a]	pH	Clarity[a]	pH	Clarity[a]
Fe^{3+}	25	--	--	--	--	--	--	6.8	0
	50	--	--	6.6	0	6.9	0	5.9	5
		Herc.	0.75	6.8	0	6.6	0	--	--
	100	--	--	5.0	0	5.7	4	4.2	4
		Herc.	0.75	5.6	3	5.6	4	4.3	4
	150	--	--	--	--	4.5	1	3.4	3
		Herc.	0.75	--	--	4.3	1	3.4	3
Alum[b]	100	--	--	--	--	9.0	0	--	--
		Herc.	0.75	--	--	8.6	0	--	--
	200	--	--	--	--	8.4	1	--	--
	300	--	--	--	--	7.2	4	--	--
Alum[c]	200	--	--	7.4	1	--	--	--	--
	300	--	--	7.1	5	--	--	--	--
	400	--	--	6.5	4	--	--	--	--
Alum[d]	200	--	--	7.0	1	--	--	--	--
	300	--	--	6.9	5	--	--	--	--
	400	--	--	6.5	4	--	--	--	--

[a] Clarity: 0 = untreated control
1-5 = partial to complete clearing of the supernatant after one hour settling.

[b] Analytical grade.

[c] Commercial grade with precipitate in suspension.

[d] Commercial grade decanted to remove the precipitate.

Tests on Combined Locks Mill Effluent

Since Mill F had been one of those in the preliminary jar test studies on the optimization of soluble BOD_5 removal, only a few additional tests were conducted prior to the pilot-scale field trials. Data from these tests (Table 25) substantiated the earlier findings (Tables 15 and 16) that ferric chloride, ferric sulfate and alum were all effective in removing total and soluble BOD_5 from this waste stream. We found, however, marked variations in the amounts of removal with the different concentrations and combinations of the flocculants used, apparently depending upon the amounts of spent cooking liquor in the mill effluent.

TABLE 22. JAR TESTS OF THE EFFECT OF FLOCCULANTS ON pH, BOD$_5$, COD, AND COLOR OF EFFLUENTS FROM MOSINEE CLARIFIERS[a]

			Reduction, %			
Flocculant			Total			Soluble
Type	mg/l	pH	BOD$_5$	COD	Color	BOD$_5$
From North Clarifier:						
FeCl$_3$	50[b]	5.1	61	72	65	39
	100	3.4	63	72	79	40
	150	3.0	64	68	85	38
Alum	100	6.0	43	56	42	26
	200	6.2	61	70	65	25
	300	6.2	61	70	68	26
Lime	200	9.9	25	32	28	-14
	300	11.1	33	48	42	-19
	500	11.6	41	55	42	0.8
Hercofloc 812.3	0.75	8.8	12	4	7	-6
	1.5	8.6	15	11	4	3
From South Clarifier:						
FeCl$_3$	50[b]	5.7	63	68	46	38
	100	3.8	65	70	70	39
	150	3.1	59	64	75	38
Alum	100	6.9	No flocculation			
	200	6.5	60	64	27	31
	300	5.6	62	66	46	26
Lime	200	11.3	No flocculation			
	300	11.6	43	44	2	-13
	500	12.0	43	50	11	3
Hercofloc 812.3	0.75					
	1.5		No flocculation			

[a] Initial values (control) of samples taken 11/21/74:

	North	South
Soluble BOD (mg/l)	North=124	South=130
Total BOD (mg/l)	North=214	South=240
COD (mg/l)	North=628	South=612
Color (units)	North=108	South=63.

[b] As Fe^{3+}.

TABLE 23. EFFECT OF pH ON JAR TEST FLOCCULATION OF MOSINEE CLARIFIER INFLUENT[a]

Primary flocculant (mg/l)		Final pH	BOD_5 reduction, %		Reduction in suspended solids, %
			Total	Soluble	
Fe^{3+}	50	10.7	-3	-5	22
	100	10.3	-5	-3	55
	150	9.9	1	6	72
	200	9.4	--	8	50
Alum	200	10.8	-0.2	1	35
	300	10.6	-7	4	18
	400	10.4	4	12	2
	500	10.2	2	7	15
	600	10.1	2	5	30
Influent adjusted to pH 8 with sulfuric acid prior to jar test:					
Fe^{3+}	50	7.2	6	11	75
	100	6.8	6	4	72
Alum	200	7.5	-9	5	76
	300	7.3	-5	-7	84
	400	7.1	-8	20	80

[a] Influent sample of 2/11/75 had an initial pH of 11.2.

The effect of these spent liquors and other mill discharges on the overall efficiency of the clarifier is discussed in Section VII.

LABORATORY SURVEY OF SOURCES OF SOLUBLE BOD_5 IN MILL SYSTEMS

In a mill system with multiple sewers there are certain streams that carry the bulk of the BOD and COD. Some of the BOD and COD can be more easily removed from concentrated streams than from diluted waste, and some substances may alter the properties of others or interfere with their removal. Therefore, isolation and treatment of these more concentrated streams would be a logical way to improve the removal of BOD_5 by the clarifiers and thereby reduce the BOD_5 load on the out-plant treatment system. Importantly also, the degree of recycling of the process water could be substantially increased.

Separate Sewer Discharges

In our study samples from the separate sewer discharges were obtained from two of the mills and analyzed for various types of solids, for soluble and total BOD_5, as well as soluble and total COD components (Tables 26 and 27).

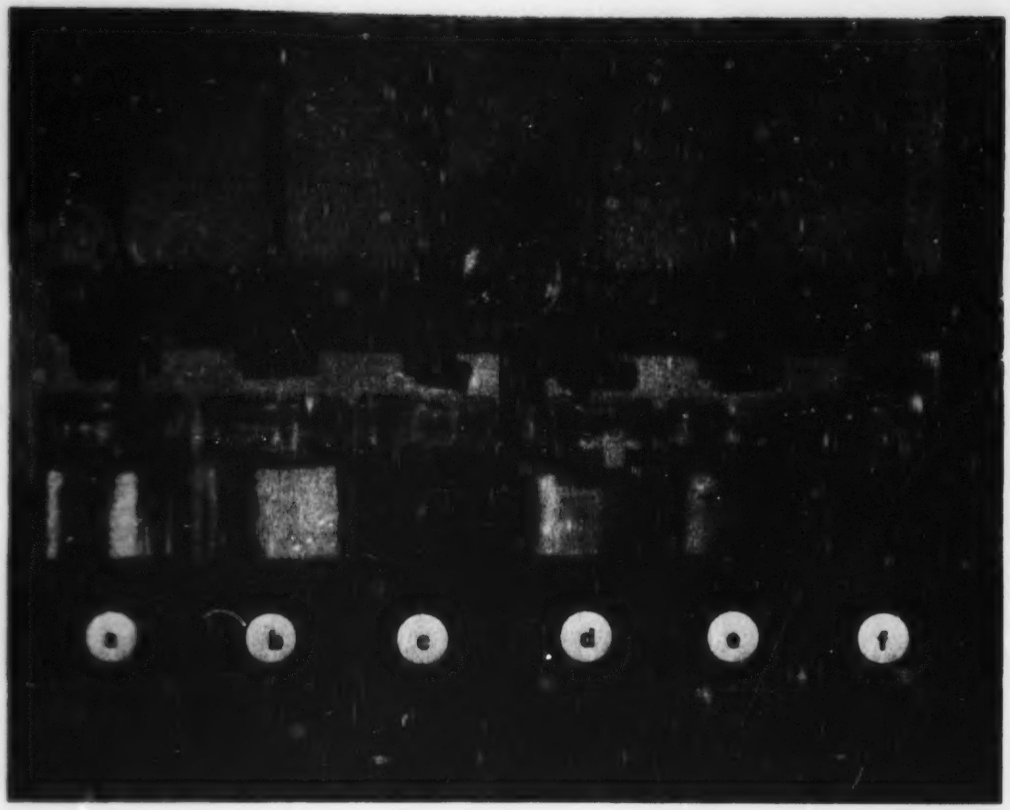


Figure 7. In jar tests with Mosinee mill effluent, pH 8.5, ferric chloride and ferric sulfate at 25 and 50 mg/l of Fe^{3+} (a), (b), (d), and (e), precipitated more solids than when they were used at a higher concentration, 100 mg/l of Fe^{3+} (c) and (f).

If one or more of the high BOD_5 streams (the discharges from the CM sewer in Mill F or the pulp mill, soda recovery or fifth stage brownstock washer sewers in Mill K) could be treated separately by flocculation, reverse osmosis, ultrafiltration or some other process, the overall efficiency of the treatment plant would increase, there would be less of a load on secondary facilities, and there would be a greater potential for water reuse (details discussed in Section VII).

Breakdown of Fibers

Another source of soluble BOD_5 was fibers: saccharides and other microbial nutrients are released during the beating of pulp or during the recycling of fibers in water recovery systems.

In order to study this release of soluble BOD_5, a beater test was arranged with a sample of unbleached sulfite pulp in a laboratory beater using a conventional 1-1/2 pound (0.68 kg) test with 12 pounds (5.5 kg) on the bedplate. One-liter samples were removed at half-hour intervals during the 90-minute test period and freeness, total solids, total and soluble BOD_5, and total and soluble COD were analyzed on each sample (Table 28).

TABLE 24. VOLUME OF SLUDGE FROM MOSINEE CLARIFIER INFLUENTS TREATED WITH VARIOUS FLOCCULANTS AND POLYMER

Flocculant						
Primary, mg/l		Polymer,[a] mg/l		Sludge volume, ml/l	Final pH	Clarity[b] 0-5
Influent 12/21/74:						
Fe^{3+}	50	None	--	122	5.4	4
	50	Herc.	0.75	115	5.5	5
Alum	100	None	--	64	6.2	2
	100	Herc.	0.75	54	6.5	2
Influent 12/31/74:						
Fe^{3+}[c]	50	None	--	92	6.3	4
	50	Herc.	0.75	80	6.2	5
Fe^{3+}[d]	50	None	--	96	6.3	5
	50	Herc.	0.75	85	6.3	5
Influent 1/16/75:						
Fe^{3+}	50	None	--	36	6.6	0
	50	Herc.	0.75	30	6.8	0
	100	None	--	48	5.0	0
	100	Herc.	0.75	60	5.6	3
Alum	300	None	--	96	6.3	4
	300	Herc.	0.75	80	6.3	5

[a] Herc., Hercofloc 812.3.
[b] Clarity: 0 = control (no apparent flocculation)
5 = clear supernatant.
[c] Analytical reagent grade of $FeCl_3$.
[d] Commercial grade, 42°Be, of $FeCl_3$.

Soluble BOD_5 and soluble COD markedly increased as the beating progressed and the fibers were fibrillated, releasing materials which became microbial nutrients in the BOD_5 test.

We ran several flocculation tests on portions of the filtrate from a 90-minute beaten sample (D in Table 28). This sample was passed through a 0.45-µm filter to remove fibers and insoluble BOD_5 and COD components. Ferric chloride was again the best "single" flocculating agent (51 percent removal

TABLE 25. REMOVAL OF BOD_5 FROM EFFLUENTS OF COMBINED LOCKS MILL BY FLOCCULANTS AND POLYMERS

Flocculant				Effluent 4/23[b]		Effluent 4/24[c]	
				BOD_5 removal, %		BOD_5 removal, %	
Primary, mg/l		Polymer,[a] mg/l		Total	Soluble	Total	Soluble
$FeCl_3$[d]	10	None	--	No flocculation		--	--
	25	None	--	No flocculation		--	--
	50	None	--	--	--	18.9	15.5
	50	H812.3	0.75	--	--	18.5	14.4
	50	N73C32	1.0	--	--	30.6	26.3
	75	None	--	38.3	30.9	29.7	20.1
	75	N73C32	1.0	36.9	21.8	27.5	23.7
	75	H813.2	0.75	--	--	26.1	18.6
	100	None	--	42.0	30.4	--	--
$Fe_2(SO_4)_3$[d]	25	None	--	No flocculation		--	--
	37.5	None	--	No flocculation		--	--
	50	None	--	No flocculation		36.9	27.8
	50	H812.3	0.75	--	--	26.6	16.0
	50	N73C32	1.0	--	--	29.3	20.1
	75	None	--	26.1	20.6	22.5	9.8
	75	H812.3	0.75	--	--	38.7	28.4
	75	N73C32	1.0	--	--	32.0	35.6
Ferri-floc[d]	75	H812.3	0.75	--	--	26.6	14.4
	75	N73C32	1.0	--	--	20.7	15.5
Alum	50	None	--	No flocculation		--	--
	100	None	--	No flocculation		--	--
	200	None	--	--	--	8.1	13.9
	300	None	--	--	--	25.2	10.3
Lime	200	H812.3	--	No flocculation		--	--
	200	N73C32	--	No flocculation		--	--
None	--	H812.3	0.75	--	--	5.4	-6.7

[a] H812.3, Hercofloc 812.3; N73C32, Nalco 73C32.

[b] 4/23 BOD_5: Total = 274 mg/l
Soluble = 220 mg/l.

[c] 4/24 BOD_5: Total = 222 mg/l
Soluble = 194 mg/l.

[d] As Fe^{3+}.

TABLE 26. SOURCES OF SOLUBLE AND TOTAL COD AND BOD_5 IN EFFLUENTS OF MILL F[a]

Source	Flow, mgd	pH	Solids					COD			BOD_5		
			Suspended		Dissolved		Total, mg/l	Soluble		Total, mg/l	Soluble		Total, mg/l
			mg/l	% Total	mg/l	% Total		mg/l	% Total		mg/l	% Total	
Main sewer	3	7.63	860	51.9	796	48.1	1656	309	29.4	1052	119	47.4	251
CM sewer	1.3	7.75	2322	59.2	1598	40.8	3920	1284	69.8	1838	585	100.5	582
Wrapper room	1.2	7.58	620	61.1	394	38.9	1014	172	17.1	1006	35	24.0	146
No. 6 sewer	0.95	7.60	1618	69.9	698	30.1	2316	122	8.8	1394	28	15.5	181
Clarifier influent	7.4	7.63	972	46.0	1140	54.0	2112	453	30.5	1486	190	52.9	359

[a]Samples taken 9/10/74.

TABLE 27. CHEMICAL, BIOLOGICAL, AND PHYSICAL ANALYSES OF VARIOUS PROCESS STREAMS WITHIN THE MOSINEE MILL (MILL K)

Source	pH	Total, mg/1		Soluble, mg/1[a]		Color[b]	Suspended solids[c]	
		COD	BOD_5	OC	BOD_5		0.45 µm	5 µm
Digester sewer	11.8	2971	635	741	775	4000	239	98.5
Pulp mill sewer	11.2	4460	1624	1099	1074	4880	260	71
5th Stage brownstock washer	10.7	4865	1349	1402	1156	4150	130	94
High density sewer	9.7	553	158	138	144	920	120	26
Foul evaporator condensate	8.5	871	762	197	624	100	22	34
Digester blowdown foul condensate	8.2	1485	964	389	953	562	2	15
Soda recovery sewer	10.1	8328	4162	2077	3705	4200	636	184
Clarifier influent	8.0	920	181	74	106	92	1004	686

[a] Passing through a 0.45 µm Metricel filter.

[b] Co-Pt units at 465 nm (NCASI Method).

[c] Collected on filters of 0.45 and 5 µm pore size.

of soluble BOD_5) (Table 29). We added cellulose powder (500 mg/l, Whatman, Standard grade) to provide particles of high surface area and enhance flocculation (No. 3 series in Table 29); it slightly increased the removal of soluble BOD_5 (1-9 percent). At pH 7.7 with alum, the removal was 2 percent better than at pH 4.2 (2A versus 1A). The addition of cellulose powder and a pH of 7.7 further increased (to 9 percent) the soluble BOD_5 that was removable with 200 mg/l alum. A combination of cellulose, lime and alum at pH 10.7 (4C) was 23 percent better than lime alone at pH 11.8 (1C) or lime and alum without cellulose (2C) at pH 10.7 (29 percent increase). Additional work on the effect of these high BOD_5 streams on the efficiency of clarifiers was done later in the study and is discussed in greater detail in Section VII.

TABLE 28. RELEASE OF SOLIDS, SOLUBLE COD, AND BOD_5 BY BEATING[a]

Sample no.	Beating, min	Freeness, ml[b]	24 Hr solids, g/l	Soluble COD mg/l	Soluble COD Increase, %	Soluble BOD_5 mg/l	Soluble BOD_5 Increase, %
A	0	750	0.29	334	--	77	--
B	30	370	0.32	396	18.6	77	0
C	60	100	0.35	416	24.6	118	53.2
D	90	30	0.38	462	38.3	128	66.2

[a] 1-1/2 lb beater method with 5.5 kg load on the bed plate.

[b] Canadian standard.

ALTERNATE METHODS FOR REDUCTION OF BOD_5

Ultrafiltration is a process for the separation of soluble low and high molecular weight (or size) components into two separate streams through the use of semiselective membranes under low pressure (less than 300 psig or 21 kg/sq cm). We used ultrafiltration in two trials with effluents from Mill F.

In the first trial a sample of the total mill discharge to the clarifier was processed through a Westinghouse module using a polysulfone membrane that had high pH and temperature limits (pH 11.5 and 95°C). Removal of 59-65 percent of the soluble BOD_5 was attained in the permeate (that portion of the solution passing through the membrane). The permeate apparently contained low molecular weight components, such as acetic acid, that had not been removed by flocculating agents (Table 30, Part A). The flocculating agents, lime with the polymers Nalco 609 or Dow PAA (polyacrylamide) did not remove additional soluble BOD_5 from the permeate of the total mill effluent.

The second trial (Table 30, Part B) was conducted with a sample of the CM sewer effluent, which had been shown in previous work to contain 33 percent of the soluble BOD_5 in 18 percent of the flow going to the clarifier.

Ultrafiltration without additives removed 69 percent of the soluble BOD$_5$, and activated carbon did not remove any more BOD$_5$. Apparently the membrane was the controlling factor in the removal of soluble BOD. The carbon did not adsorb any of the transferrable components probably because its adsorptive capacity was used up by larger, more heavily charged molecules.

TABLE 29. JAR TESTS OF VARIOUS FLOCCULATION TREATMENTS OF FILTERED 90-MINUTE BEATER SAMPLES[a]

Treatment and sample	Flocculant		pH	Soluble COD		Soluble BOD$_5$	
	Type	mg/l		mg/l	Reduction, %	mg/l	Reduction, %
1. Flocculant added:							
A	Alum	200	4.2	458	2.1	105	0.0
B	FeCl$_3$	200	2.7	256	45.3	51	51.0
C	Lime	200	11.8	449	4.0	98	5.8
2. Above samples treated with alum and flocculated:							
A	Alum	200	7.7	336	28.2	102	1.9
C	Alum	200	10.7	449	4.0	109	0.0
3. Cellulose powder (500 mg/l) added to No. 1 samples:							
A	Alum	200	4.2	400	14.5	95	8.6
B	FeCl$_3$	200	2.7	248	47.0	50	51.9
C	Lime	200	11.8	422	9.8	90	13.5
D	Control	None	--	468	—	104	--
4 Alum added to No. 3 samples:							
A	Alum	200	7.7	355	22.0	88	15.4
C	Alum	200	10.7	406	13.2	74	28.8

[a] Initial values: pH = 6.7
Soluble COD = 462 mg/l
Soluble BOD$_5$ = 128 mg/l.

TABLE 30. SOLUBLE COD AND BOD_5 IN MILL F EFFLUENTS TREATED WITH FLOCCULANTS AND REVERSE OSMOSIS OR ULTRAFILTRATION

Stream	Flocculants		Membrane treatment	Sample	Soluble COD		Soluble BOD_5	
	Type	mg/l			mg/l	Reduction, %	mg/l	Reduction, %
A. Clarifier influent	None	--	UF	Feed	433	--	220	—
				Permeate	136	68.6	78	64.5
	Lime + Nalco 609	300 0.5	UF	Feed	382	—	180	--
				Permeate	138	63.9	73	59.4
	Dow PAA	10.0	UF	Feed	433	—	206	--
				Permeate	138	68.1	73	64.6
B. CM sewer	None	--	UF	Feed	1095	--	528	—
				Permeate	292	73.3	162	69.3
	Activated carbon	200	UF	Feed	901	--	426	—
				Permeate	218	75.8	137	67.8
	None	--	UF + RO	Feed	1095	--	506	--
				Perm. UF	392	64.2		
				Perm. RO	58	94.7	38	92.5
	None	--	RO	Feed	1196	--	522	—
				Permeate	98	91.8	57	89.1
	None	--	UF + RO	Feed	1039	--	489	—
	None	—		Perm. UF	306	70.5		
	A/C	200		Perm. RO	36	96.5	31	93.7
	$FeCl_3$	100 (as Fe^{3+})	UF	Feed	795	--	508	—
				Permeate	297	62.6	180	64.6

The ultimate value of ultrafiltration might be in concentrating the high molecular weight soluble BOD_5 components and removing them from process streams. It has been demonstrated elsewhere (21) that ultrafiltration could be carried to a concentration of 25-35 percent solids without complications from osmotic pressure buildup which directly affects RO flux rates and concentrations. This would be sufficiently high for final disposal by discharge into the strong pulping liquor streams for evaporation and utilization or burning. Still another use for ultrafiltration is in reducing the buildup of high molecular weight solubles in recycled process water within the mill; this could reduce water consumption and the volume of overflow to the outplant clarifier.

Reverse osmosis, similar to ultrafiltration but operating at higher pressures (400-800 psig or 28-56 kg/sq cm) with tighter membranes which reject smaller molecules, was tried both as a possible treatment method and as a further refinement for the permeate from the ultrafiltration process (see Table 30). The soluble BOD_5 removal of 89 percent for reverse osmosis alone was increased to 92 and 94 percent, respectively, by either the ultrafiltration pretreatment or the addition of activated carbon to the reverse osmosis feed. The advantageous use of activated carbon in the reverse osmosis feed, which had been pretreated by ultrafiltration, substantiates the previous conclusion that the high molecular weight materials of the ultrafiltration feed were utilizing or plugging all of the available adsorptive sites on the carbon.

Ferric chloride was added to the ultrafiltration feed in order to develop a floc and possibly increase membrane rejection and soluble BOD_5 removal. Ferric chloride actually worked in reverse and increased the transfer of soluble BOD_5 through the membrane. This loss of membrane rejection reduced the removal of the soluble BOD_5 components by 4 percent. Subsequent tests indicated that the ferric ion did not damage the membrane: after the module was washed with detergent, it gave salt (NaCl) rejection comparable to those for a new membrane.

SECTION VI

PILOT SCALE CLARIFIER STUDIES

GENERAL

The information from jar test studies of the effluents from the Mosinee and Combined Locks mills were used to prepare a scheme for the treatment of these mill effluents with a pilot-scale clarifier.

This clarifier had been developed at The Institute of Paper Chemistry under Project 3029, jointly sponsored by member companies of the Institute, the Environmental Technology Corporation (ENCOTEC) and the Upper Great Lakes Regional Commission (12). The stainless steel cone of the clarifier had a center height of 1.3 meters (4.25 feet) and a diameter of 1.1 meters (3.5 feet). The inlet was downflow through a 5.1-cm (2-inch) stainless steel pipe with an opening 40 cm (1.25 feet) from the bottom of the cone. It was equipped with an overflow weir which discharged into a 5.1-cm (2-inch) trough around the entire circumference of the top.

This section of the report covers the initial laboratory "shakedown" studies, the on-site studies at the mill in Mosinee, Wisconsin from January 15 to April 4, 1975, and the on-site studies at the mill in Combined Locks, Wisconsin from April 8 to June 26, 1975.

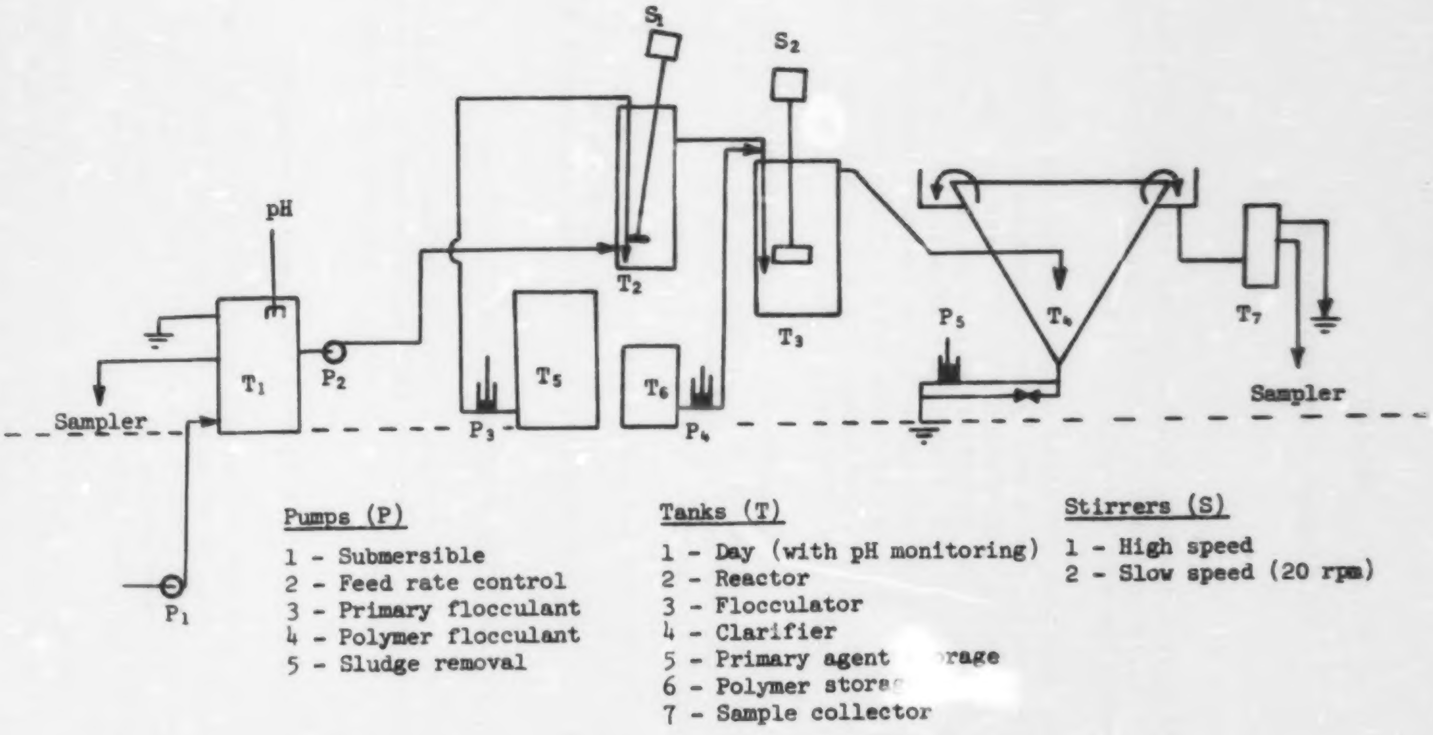
The problems encountered and some of the solutions developed for the correction of these problems are discussed. Data are given and discussed for the removal rates attained for suspended solids, total and soluble BOD_5 and color.

TRIALS WITH THE PILOT CLARIFIER UNDER LABORATORY CONDITIONS

Three thousand gallons of Mosinee clarifier influent were delivered by truck to the Institute early in January 1975 and were used to check the operation of the clarifier system (Figure 8) without the samplers or the submersible pump (P-1).

The system consisted of the following items and arrangement:

1. A tank (T-1) provided a constant supply of waste to be treated.
2. A feed control pump (P-2) maintained a constant feed rate.
3. A 35-liter (9-gallon) reactor tank (T-2) with a high speed mixer provided rapid mixing of the waste with the primary flocculating agent and permitted gravity flow to the balance of the stream.
4. The flow from the reactor tank was into an open pipe extending to the bottom of the flocculator tank (T-3). If polymer was to be added, it was introduced at the top of this open pipe,


pH
S1
S2
T1
T2
T3
T4
T5
T6
T7
P1
P2
P3
P4
P5
Sampler
Sampler

Pumps (P)

1 - Submersible
2 - Feed rate control
3 - Primary flocculant
4 - Polymer flocculant
5 - Sludge removal

Tanks (T)

1 - Day (with pH monitoring)
2 - Reactor
3 - Flocculator
4 - Clarifier
5 - Primary agent storage
6 - Polymer storage
7 - Sample collector

Stirrers (S)

1 - High speed
2 - Slow speed (20 rpm)

Figure 8. Schematic of pilot-scale clarifier installation.

into a quiescent zone approximately one-quarter of the distance down the pipe in order to provide adequate mixing without excessive turbulence or floc dispersion. In the center of this tank was mounted a slow speed (20 rpm = 1.6 fps peripheral velocity) paddle that mixed without excessive shear.

5. The overflow from the flocculator tank passed downflow into the clarifier (T-4), with the flow from the weir trough into a small sampling pot (T-7) and then to the sewer.
6. In these laboratory studies the sludge was removed from the bottom of the clarifier by gravity flow through a vented overflow pipe (not shown) that could be raised and lowered to control the rate of flow. Both gravity flow and a pumping system were used in the field trials and are discussed in the following part of this section.
7. The flocculating agents were stored in small tanks (T-5,6) and were metered into the system with tubing pumps (P-3,4).

We used this equipment to do a brief laboratory study of the effects of waste flow and sludge removal rates, at a constant level of flocculating agent(s), on the quality of the discharge produced. An excellent quality discharge (Table 31) appeared to be produced if the waste feed and the sludge discharge rate resulted in an overflow rate of 140-150 liters per square meter per day (400-425 gallons per square foot per day). The removal also appeared to be dependent upon the type of sludge blanket developed in the clarifier. Best results were obtained with the level at least five centimeters (2 inches) from the top to prevent floc carryover, but not less than one meter (3 feet) from the bottom; i.e., 60 cm (2 feet) above the waste inlet. This arrangement seemed to promote the development of larger floc particles and a filtration effect to markedly enhance the quality of the discharge. These parameters were, therefore, selected for the operation of the unit during the field trials.

EQUIPMENT AND OPERATION AT MOSINEE PAPER CORPORATION

The IPC system was to be operated in parallel with the two mill clarifiers and was, therefore, installed in the waste treatment plant in a concrete building. This building was immediately adjacent to the two commercial clarifiers and was unheated, except for heat from the incoming waste stream.

Due to the arrangement of the waste stream flow pattern, it was necessary to use a submersible pump (P-1 in Figure 8), mounted in the waste treatment trench immediately downstream from the bar and traveling screens, to lift the waste to floor level (2-2.5 meters or 6-8 feet) at a rate of 19-30 liters (5-8 gallons) per minute.

The flow from the submersible pump was directed into the bottom of a 190-liter (50-gallon) stainless steel tank (T-1) for supplying a centrifugal feed pump (P-2) with the excess overflowing to the sewer near the influent sampler. This tank also contained the pH recording equipment.

The feed pump (P-2) maintained a waste flow of 11.4 liters per minute (3 gpm) into the reactor tank (T-2), and the only other modification of the equipment, over that described in the laboratory trials, was the installation of a pump in the sludge removal line during some of the trials.

TABLE 31. LABORATORY EVALUATION OF PILOT-SCALE CLARIFIER[a]

Overflow rate[b]	Sludge removal, %	Flocculant, mg/l		% Removal of			
		Primary Fe^{3+}	Polymer H812.3	Suspended solids	Color	BOD_5 Total	BOD_5 Soluble
369	20	87	1.3	99	55	24	8
395	13	64	0.78	99	79	34	17
406	10	61	0.77	99	--	29	9
425	10	52	0.77	97	46	36	10
526	15	51	0.77	19	49	19	13
579	12	51	0.77	-52	49	5	16
587	10	50	0.77	-29	48	0	0
632	14	50	0.75	-35	49	9	9

[a] Initial (control) values: Suspended solids = 234 mg/l
Total BOD_5 = 134 mg/l
Soluble BOD_5 = 114 mg/l
Color = 130 units.

[b] Overflow in gallons/square foot/day based on surface area of clarifier.

SAMPLING AT MOSINEE PAPER CORPORATION

During the first part of the mill study, influent and effluent samples were taken with two Model WM-5-24R refrigerated Sigmamotor samplers (Sigmamotor, Inc. of Middleport, New York) set to take individual samples hourly around the clock. In order to reduce the analytical load, these were composited into 12-hour samples daily.

It soon became apparent that the rapid changes in mill discharge (Table 32 and Figure 9) would not permit such an infrequent sampling scheme. A third sampler, a CVE refrigerated unit (Quality Control Equipment Company of Des Moines, Iowa) capable of taking small samples at short intervals (1-60 minutes) for compositing in a 4-liter (1-gallon) bottle, was placed in the influent stream. This unit was set to take 40-ml samples at 15-minute intervals and the 12-hour composites were compared with those from one of the Sigmamotor units taking 400-ml aliquots from the same influent.

Poor correlation was evident (Table 33) and a second trial was made. This was with four samplers in the following arrangement:

a. The two Sigmamotor samplers on the influent and effluent streams set at 30-minute intervals, taking 24 400-ml samples in 12 hours.

b. The CVE sampler on the influent line taking a 40-ml sample every 10 minutes.

c. A polystaltic tubing pump (Buchler Instruments of Fort Lee, New Jersey) set to take 9 ml per minute continuously was used on the effluent line.

TABLE 32. ANALYSIS OF INDIVIDUAL SAMPLES TO ESTABLISH RANGE[a]

No.	pH	Milligrams/liter Suspended solids	Total BOD_5	Soluble BOD_5
1	10.12	210	241	203
2	10.07	628	206	178
3	9.57	494	166	138
4	9.63	145	155	138
5	9.11	85	129	116
6	9.48	144	135	114
7	8.86	265	143	140
8	9.40	152	163	140
9	9.19	97	148	140
10	9.30	76	127	117
11	9.78	94	138	135
12	9.60	115	132	124
13	9.59	267	148	118

[a] Samples taken at hourly intervals (start 10 a.m. 1/16/75).

Analytical comparisons were excellent (Table 34) and indicated that the Sigmamotor samplers could be used to take representative samples if the 30-minute cycle was used.

In order to compensate for the "system holdup time" of 90 minutes, the samples were composited to obtain representative samples from the same 12-hour test period. This was readily accomplished by compositing the individually numbered bottles in groups so that those from the effluent were three bottles "behind" those for the influent.

Samples of the mill clarifier influent and effluent were taken at 7:30 a.m. daily by the mill staff and analyzed by both mill and IPC personnel.

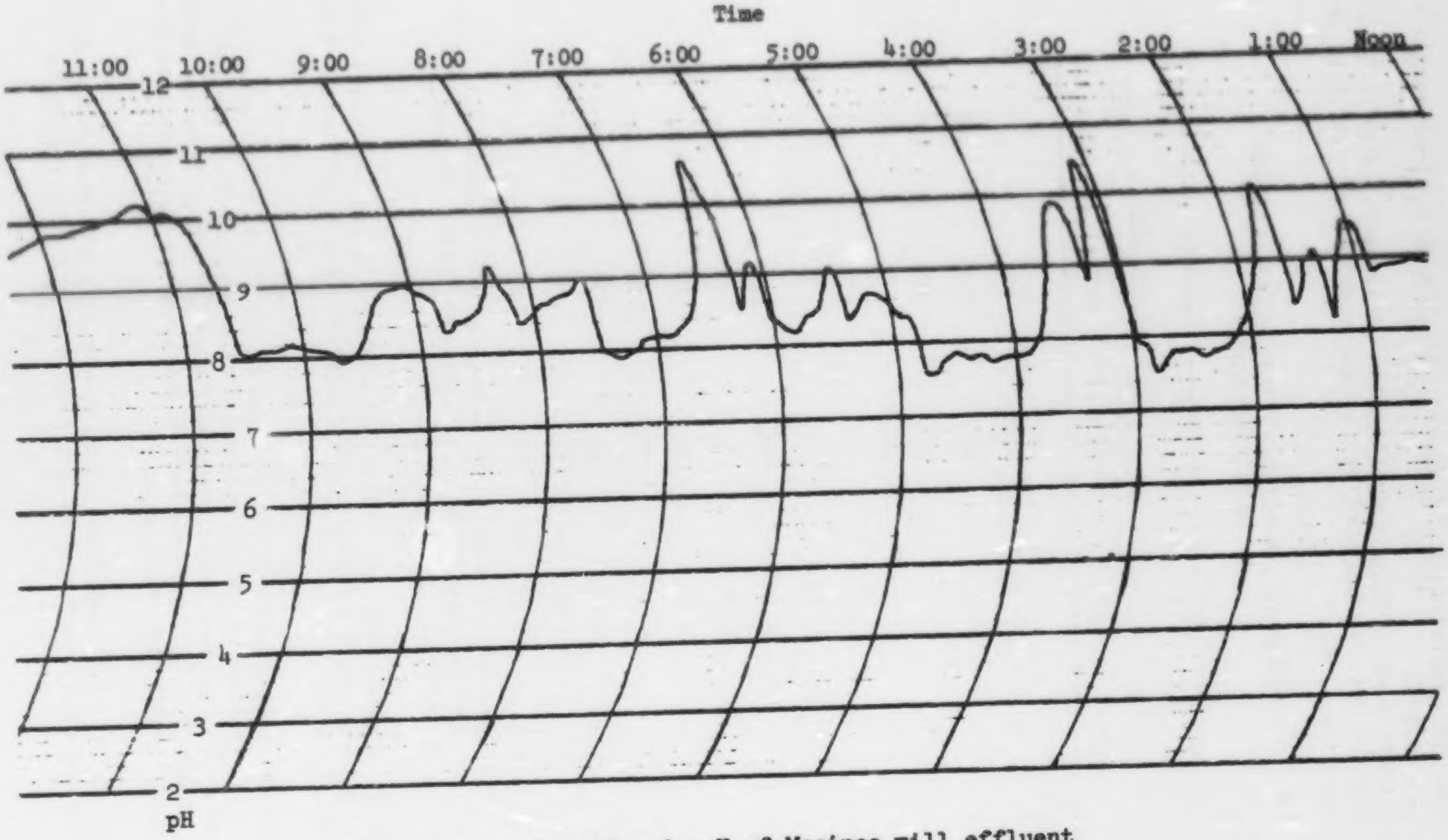


Figure 9. Variation in pH of Mosinee mill effluent entering pilot-scale clarifier.

TABLE 33. ANALYSIS OF SPECIAL AND REGULAR SAMPLES OF CLARIFIER INFLUENT, TRIAL NO. 1[a]

			Mg/1							
	pH		Suspended solids		Total BOD_5		Soluble BOD_5		Pt-Co color	
No.	Special	Regular	Special	Regular	Special	Regular	Special	Regular	Special	Regular
1	7.22	7.85	219	189	162	190	88	93	38	78
2	7.82	8.75	182	136	177	244	109	138	115	130
3	8.05	7.73	221	126	130	128	102	88	119	133
4	8.40	8.51	210	199	124	158	108	117	170	204
5	7.48	8.40	257	240	104	140	84	95	67	168
6	7.35	7.61	213	169	98	142	76	88	45	74
7	7.35	7.11	213	198	120	88	94	86	60	82

[a] Special sample: A composite of 40-ml samples taken with a CVE sampler every 15 min for 12 hours; regular sample: a composite of 400-ml samples taken with a Sigmamotor sampler every hour for 12 hours.

TABLE 34. ANALYSIS OF SPECIAL AND REGULAR SAMPLES OF CLARIFIER INFLUENT, TRIAL NO. 2[a]

Sample No.		pH			Total BOD_5, mg/l			Soluble BOD_5, mg/l			Color (Pt-Co units)		
Special	Regular	Special	Regular	Mill	Special	Regular	Mill	Special	Regular	Mill	Special	Regular	Mill
AA-1	A-1	8.08	8.09	7.70	197	180	186	162	148	149	268	273	143
AA-2	A-2	7.41	7.22		174	173		120	124		95	145	
BB-1	B-1	4.41	4.67	-	128	122	-	116	107	-	42	45	-
BB-2	B-2	3.69	3.61		94	86		90	83		65	52	
AA-3	A-3	7.61	7.40	7.33	183	165	170	142	135	116	120	122	90
AA-4	A-4	7.19	7.20		140	139		110	104		50	68	
BB-3	B-3	3.99	3.96	-	111	106	-	101	98	-	22	55	-
BB-4	B-4	3.30	3.32		95	89		90	86		50	70	

[a] All samples composited on a 12-hour basis.

[b] A and B: A composite of 400-ml samples taken by Sigmamotor samplers at 30-minute intervals on influent and effluent.

AA: A composite of 40-ml samples taken by a CVE sampler at 10-minute intervals on influent.

BB: Continuous sample taken by a polystaltic pump at 9 ml/min from the effluent.

No. 1 & 3: 7:00 a.m. to 7:00 p.m.
No. 2 & 4: 7:00 p.m. to 7:00 a.m.
Mill: 7:30 a.m. composite.

For analysis all samples for BOD_5 were stored at 4°C (40°F) and the others were maintained at room temperature.

TESTING SCHEDULE AT MOSINEE CORPORATION

In order to establish a comparison between the mill and IPC clarifiers, the first trial was the operation of the pilot unit under conditions as near those of the mill as practical. Since we were not attempting to develop optimum clarification at high hydraulic loadings, but merely to study the increased removal of the soluble BOD_5 from the waste stream while operating under different chemical treatment conditions, it was not necessary to show that we could exactly duplicate mill operation. Rather, it was more important to show that any increase in BOD_5 removal was due to the chemical additives and not to the clarifier design alone.

We developed a "base line" by operating the IPC unit with Hercofloc 812.3 at 0.75 mg/l and with a waste flow rate of 11.4 liters/min (3 gpm) in parallel with the two mill clarifiers. The Hercofloc addition duplicated mill treatment. If a 10 percent sludge withdrawal could be maintained, the pilot clarifier overflow would be 1.6 liters per sq cm per day (400 gallons per sq ft per day), approximately one-half that of the commercial unit.

The efficiency for removal of BOD_5 in the small unit was slightly less than for the mill units under the same conditions and time period. This indicated that the design of the IPC clarifier did not promote more removal and that any increases found in later trials using chemical additive would be directly attributable to the chemical treatment.

Following the development of the base line, other chemical treatment schemes based on the laboratory studies were tested:

A. Base line using 0.75 mg/l Hercofloc 812.3.
B. Alum at 200 mg/l plus 0.75 mg/l Hercofloc 812.3.
C. Ferric chloride at (100 mg/l as Fe^{3+}) plus 0.75 mg/l Hercofloc 812.3.
D. Ferric sulfate (50-100 mg/l Fe^{3+}) without the polymer.
E. A second base-line study with the Hercofloc.
F. Sulfuric acid for pH adjustment only.
G. Sulfuric acid for pH adjustment plus the Hercofloc.
H. Ferrous sulfate (100 mg/l Fe^{2+}) plus 0.75 mg/l Hercofloc.

The original plan was to have tests of two weeks' duration. Unfortunately, the several periods of problem and solution development we encountered early in the study delayed the program and resulted in shortened test periods (for F, G, and H, above) near the end of the study. Also, throughout almost the entire trial period, the Mosinee mill was on a reduced work week (4 days), which limited the operation of the small clarifier to the period between 9:00 a.m. Tuesday and 4:00 a.m. Saturday, thereby limiting the number of samples per week.

RESULTS AND DISCUSSION OF WORK AT MOSINEE

In our first attempt to establish the base line, we immediately encountered three problems:

The first problem related to the submersible, centrifugal sump pump installed in the waste trench. It had a small 2.5-cm (1-inch) inlet hole in the baseplate and due to the high fluid velocity in the waste trench, an "aspirator" effect developed across the inlet when the pump was vertically mounted, and we were unable to pump sufficient waste. Mounting the pump at a 90° angle pointed downstream increased the aspiration effect, while mounting it pointed upstream resulted in rapid plugging of the inlet hole with pitch and debris not removed by the bar or traveling screens. This problem also extended to the centrifugal pump used for feed control.

The second problem was due to the high suspended solids content of the Mosinee waste. A centrifugal pump was the only available pump that was considered suitable for control of the flow at the 11.4 liters per minute (3 gpm) rate. A one-half inch Eastern centrifugal pump was, therefore, used to control the rate of waste fed to the clarifier unit, and at first the rate was controlled with a 1/2-inch valve on the pressure side of the pump. This rapidly plugged with pitch and fibers and resulted in erratic flow patterns.

The third problem developed in the gravity sludge removal system. Settling of the high suspended solids content rapidly overwhelmed the available space in the clarifier and resulted in solids carryover, even in the absence of chemical agents, other than the Hercofloc 812.3.

In order to reduce these problems:

1. A conical screen (20 mesh), 18 inches long by 7 inches in diameter, was installed on the submersible pump. When installed with the apex of the cone mounted upstream, the pumping action was excellent and the cone was somewhat self-cleaning. When mounted with downstream orientation, which should increase the self-cleaning aspect of the cone shape, the flow was reduced below acceptable levels. Periodic cleaning, with high pressure water, was required to maintain an adequate supply to the system.

2. The centrifugal feed pump was fitted with a smooth-bore orifice plate for flow control and with periodic cleaning this provided better flow control.

3. A multihead tubing pump (Brosites/ was installed in place of the gravity system for sludge removal. In the last four trials a throttled centrifugal pump was tried in this position and found to work the best of any of the schemes attempted.

Although none of these worked perfectly and problems were encountered from time to time, failure of the system could be minimized with careful cleaning and operation procedures.

Data for the trials with the various flocculating agents and for the base lines are summarized in Table 35. The more detailed analysis of the individual samples are in Appendix B (Figures B-1 to B-10, Tables B-1 to B-5). These data were first used to establish confidence limits, and the following summary was developed.

1. Both the initial and final trials (A and E of Table 35) with 0.75 mg/l Hercofloc 812.3 indicated, as previously noted, that the IPC unit was equal to or slightly less efficient than the mill clarifiers in removing suspended solids, soluble BOD_5 and color.

2. The reason for the marked difference noted in the total BOD_5 reductions for the mill clarifier during the second trial is unknown; throughout the study period there had been a slow, progressive increase in the efficiency of the mill clarifier in removing BOD_5; i.e., from 14 to 35 percent between Trials A and H. This was not readily traceable to changes in the concentration of BOD_5 going to the clarifiers during this period, since these were on the average 161, 120, 138, 181, 161, 211, 114 and 178 mg/liter for Trials A to H, respectively.

3. Alum with polymer and without pH adjustment, as predicted by the laboratory trials, did not increase the removal of the BOD_5 components but did markedly increase the efficiency of removal of suspended solids and color.

4. The ferric ion, both as chloride and sulfate salts, was an excellent flocculating agent for removing BOD_5, the chloride form being more effective than the sulfate for suspended solids. The chloride could have been better because the final pH was nearer to the optimum for the Fe^{3+} produced flocs (pH 4-5).

5. Ferrous ions, at the level of 100 mg Fe^{2+}/l, appeared to reduce the efficiency of the system even with the addition of polymer. While this level of ion was below that which would be theoretically required by the Schulze-Hardy rule, which states that the concentration of the counterion required to collapse the double layer and produce rapid flocculation is inversely proportional to the 6th power of the valence, it was the highest level practical during our trials due to the low solubility of the commercial grade ferrous sulfate. Based on the effectiveness of the ferric ion at 100 mg/l, the level of ferrous ion theoretically required would have been approximately 1100 mg/liter.

6. The use of sulfuric acid to decrease the pH was one process under consideration by the mill for use in the large clarifiers. A trial was, therefore, designed to test this procedure for the removal of some of the components from the waste stream in the small system; but due to the mechanical difficulties we had encountered earlier in the trial period, only a short period was available near the end of the study. Although the data were insufficient to provide reliable comparisons with mill operation, laboratory studies have shown that pH reduction to below 4.5 resulted in marked reduction in suspended solids and total BOD_5, with little effect on the soluble BOD_5 level in the effluent.

TABLE 35. VARIOUS TREATMENTS OF MOSINEE MILL EFFLUENT IN PILOT-SCALE AND MILL CLARIFIERS

	Effluent quality				Removal, %			
		BOD_5				BOD_5		
Clarifier Unit	Suspended solids, mg/l	Total, mg/l	Soluble, mg/l	Color units	Suspended solids	Total	Soluble	Color
A. Both units with Hercofloc 812.3 at 0.75 mg/l:								
IPC	86	146	129	76	70	17	14	28
Mill	58	137	129	74	80	14	13	28
B. IPC unit with 200 mg/l alum + Hercofloc 812.3 at 0.75 mg/l, and mill unit with Hercofloc 812.3 at 0.75 mg/l:								
IPC	22	96	92	21	88	19	18	81
Mill	59	98	85	89	72	18	17	46
C. IPC unit with ferric chloride (100 mg/l Fe^{3+}) and Hercofloc, and mill unit with Hercofloc only:								
IPC	16	89	80	80	90	34	23	71
Mill	62	111	91	102	72	22	8	30
D. IPC unit with ferric sulfate (50-100 mg/l Fe^{3+}) and Hercofloc, and mill unit with Hercofloc only:								
IPC	44	105	94	48	78	34	24	68
Mill	66	133	116	156	66	26	10	2
E. Second base line with both units using Hercofloc 812.3 at 0.75 mg/l:								
IPC	40	137	118	157	80	13	8	7
Mill	56	116	103	118	78	29	10	13

E, G, & H. Insufficient data to provide good comparisons.

These trials, with ferric, ferrous, and aluminum ions, and especially with the iron salts, have shown that an increase in clarifier efficiency (12 percent for total BOD_5, 15 percent for soluble BOD_5 and up to 66 percent for color) could be attained with the Mosinee waste. The sulfate form might be preferable to the chloride, particularly if the sludge were to be burned, because it is less corrosive.

One of the principal practical observations we made in the field study at this mill was on the effect of strong digester room spent liquors and washes on clarifier performance. Visual, analytical, and other evidence showed that heavy slugs and spills of these wastes — some of which lasted several hours — adversely affected clarification. A single program of grab sample collection was undertaken to help indicate the sources of strong process waters. The analytical data from the study of that one set of grab samples are summarized in Table 27, previously described, and showed the relative strength of the various soluble materials in these samples. The effects of these streams will be discussed in greater detail in Section VII.

EQUIPMENT AND OPERATION AT COMBINED LOCKS, APPLETON PAPERS DIVISION OF NCR

The clarifier equipment that had been used in the Mosinee field trials was cleaned and transferred to Combined Locks on April 7, 1975. Since it was again to be operated in parallel with the mill system, it was placed in the treatment plant building which was immediately adjacent to the two mill clarifiers. A tee was installed in the main influent line to these two clarifiers and this stream was fed into the 50-gallon day tank (T-1 in Figure 8). This eliminated the need for the submersible pump. At Mosinee we had encountered some difficulty with uneven flow over the weir of the small clarifier. Although the unit had three leveling legs, the top rim was not level around the entire periphery. Spot overflow occurred; the floc subsequently "streamed" at these points and efficiency decreased.

An adjustable leveling device for the top of the clarifier at Combined Locks was made of small strips of slotted plastic installed along the entire overflow edge. Carefully manipulated (up and down), these could be used to establish an overflow around the entire circumference. This helped to maintain a smooth top on the sludge blanket and virtually eliminated spot overflow except when the strips were disturbed during the weekly cleanup.

Two other basic changes were made for operation at the Combined Locks mill to provide better control. The high fiber content of this waste stream overwhelmed the sludge disposal system on the IPC clarifier. In order to reduce the fiber content and still retain in the influent the fine particles required for good floc formation and BOD_5 removal, we installed a side hill screen with 60-mesh wire over the top of the day tank. Later, when we encountered difficulties in maintaining a clean surface in the base-line study (A), we changed this to a Hydrasieve (C. E. Bauer, Springfield, Ohio) with 0.010 inch slots (Figure 10).

A centrifugal pump with electrical speed control was used to control the sludge level in the clarifier and the hose was clamped on the outlet side.

This was changed to run at low speed with the hose clamp removed, and the time of operation was controlled with a timed ON/OFF switch (Trial D). This permitted relatively close control of the sludge blanket level that had varied both with the "quality" of the waste fed to the system as well as with the type of flocculating agent.

Figure 10. Bauer Hydrasieve used to remove the longer fibers from the Combined Locks mill effluent

Since the level of the sludge blanket in the clarifier was apparently very important to the efficiency of the system, thought should be given to provision of a sensing type of control system for any future work with this unit.

SAMPLING AT COMBINED LOCKS

The two Sigmamotor samplers were used on the influent and effluent streams. Comparisons were again made with these two samplers, the CVE sampler and the polystaltic pump. The Sigmamotor samplers were set to take 400-ml samples every 30 minutes, the CVE sampler a 50-ml influent sample every 8 minutes, and the tubing pump a continuous 9 ml/min sample of the effluent. Samples from each were composited every 12 hours.

Data in Table 36 indicate that representative samples were taken by the Sigmamotor samplers set at the 30-minute sampling frequency. To provide for the "system hold-up" we used the same "lag period" in compositing that we used at Mosinee. Samples of the mill clarifier effluent were taken by the mill staff every morning and were analyzed at the IPC laboratories for comparison with those from the small unit. The mill had no provisions for taking 24-hour composites of the mill clarifier influent, so the influent values for the IPC clarifier for the same test period were averaged for comparison of percentage removal values for total and soluble BOD_5 and color. Since the Hydrasieve removed considerable quantities of fiber from the influent processed by the IPC unit, the removal of suspended solids could not be compared with that of the mill system.

TESTING SCHEDULE AT COMBINED LOCKS

The Combined Locks clarifier operates without chemical additives and depends upon gravity sedimentation for clarification. The "base-line" trial (Trial A) of the IPC unit was, therefore, made without chemicals. This was followed by trials:

B. Ferric chloride at 75 mg/l Fe^{3+}.
C. Ferric chloride at 75 mg/l Fe^{3+} with 0.75 mg/l Nalco 73C32.
D. Ferric sulfate at 100 mg/l Fe^{3+}.
E. Alum at 300 mg/l.
F. Alum at 300 mg/l with 0.75 mg/l Hercofloc 812.3.
G. A second base-line study with no chemical additives.

Because the IPC system was not automatically controlled and because clarifier influent quality changed rapidly on Saturdays and Sundays, we usually limited our trials to 8:00 a.m. Monday through 7:00 a.m. Saturday; several trials, however, extended through the weekend.

RESULTS AND DISCUSSION

The Hydrasieve, cleaned frequently, provided good influent for the IPC clarifier. The basic problems at this site were with plugging of the influent line between the mill main line and the 50-gallon per day tank and with the removal of sludge from the small clarifier to maintain proper sludge-

TABLE 36. ANALYSIS OF SPECIAL AND REGULAR SAMPLES OF THE CLARIFIER INFLUENT OF THE COMBINED LOCKS MILL[a]

Day	Sample no.		pH		Suspended solids, mg/l		Total BOD$_5$, mg/l		Soluble BOD$_5$, mg/l		Color	
	Special[b]	Regular[c]	Special[b]	Regular[c]	Special[b]	Regular[c]	Special[b]	Regular[c]	Special[b]	Regular[c]	Special[b]	Regular[c]
2	DD-1	D-1	8.59	8.50	62	71	291	273	270	275	170	170
	DD-2	D-2	7.68	7.70	77	74	304	296	250	251	237	237
3	DD-1	D-1	8.00	7.89	333	324	382	351	254	264	228	216
	DD-2	D-2	7.94	7.90	220	201	370	344	244	247	203	222
4	DD-1	D-1	7.76	7.70	134	104	275	285	211	216	285	287
	DD-2	D-2	7.89	7.72	191	182	280	256	224	210	240	258
5	DD-1	D-1	7.80	7.89	68	60	224	227	198	202		
	DD-2	D-2	7.80	7.71	105	97	264	256	221	201	200	192
8	DD-1	D-1	—	8.68	—	47	--	228	--	196	--	155
	DD-2	D-2	8.01	7.90	40	37	201	197	170	184	--	150
9	DD-1	D-1	8.31	8.20	59	51	250	250	214	218	--	183
	DD-2	D-2	8.03	8.01	42	41	264	286	259	228	--	170
10	DD-1	D-1	7.65	7.82	19	19	148	162	138	140	--	105
	DD-2	D-2	7.62	7.55	44	44	214	208	186	176	--	150
11	DD-1	D-1	7.71	7.62	70	66	234	240	216	211	--	217
	DD-2	D-2	7.82	7.71	35	37	272	282	249	238	--	302
12	DD-1	D-1	7.62	7.50	19	19	128	140	125	128	85	75
	DD-2	D-2	7.85	7.67	20	18	166	162	170	154	87	83
13	DD-1	D-1	7.73	7.65	32	44	264	270	256	254	225	200
	DD-2	D-2	7.68	7.71	41	31	284	286	255	271	210	205
14	DD-1	D-1	7.63	7.58	65	38	252	243	235	250	241	255

[a] All samples were composited on a 12-hour basis.

[b] Special samples: 50 ml taken by a CVE vacuum sampler at 8-min intervals.

[c] Regular samples: 400 ml taken by a Sigmamotor sampler at 30-min intervals.

blanket levels. The first remained a recurring problem throughout the study. The sludge blanket was fairly adequately maintained with the installation of the time-controlled centrifugal pump.

Data from these trials (Tables C-1 to C-7 and Figures C-1 to C-14 in Appendix C) were checked for validity (mathematical confidence limits) on the IPC computer. Averaged data for the seven trials are given in Table 37 and are summarized as follows:

1. The first base line (Trial A) showed that the IPC clarifier removed slightly more total BOD$_5$ than the mill unit did, but removed equal amounts of soluble BOD$_5$ and no color. In the second base line (Trial G) at the end of the series the units operated at equal efficiency.
2. Ferric ion, either as the chloride or sulfate salt (Trials B and D) provided excellent removal for total and soluble BOD$_5$ as well as color.
3. The addition of the polymer Nalco 73C32 (Trial C) to the ferric chloride slightly reduced the efficiency for total and soluble BOD$_5$ removal but had no effect on the color removal.
4. Alum, as predicted by the laboratory jar tests, did not appear as effective as the ferric ion in removing BOD$_5$ but was equivalent to it in reducing color.
5. The addition of the Hercofloc 812.3 polymer to the 300 mg/l alum markedly increased the removal of total BOD$_5$ to well above the level achieved with the other flocculating agents but had no effect on the reduction of the soluble BOD$_5$.

The high "negative" soluble BOD$_5$ removal in the two IPC base-line trials (Appendix C-1 and C-7), as well as throughout the test period for the mill clarifier, could not be explained. This finding, however, did correlate with the darker color of the sludge from the mill clarifiers (lighter fibrous material was in the influent waste stream) and might indicate development of both color and soluble BOD$_5$ from the "particulate matter" during clarification.

Spent liquor entering the influent system through spills or deliberate discharges had the same deleterious effect in this study at Combined Locks as it did at Mosinee. This, according to the Combined Locks mill staff, has been one of the causes of clarifier upsets that have occasionally plagued their operation. Operation of the pulp and paper mill under strict control of spills and similar discharges (i.e., good housekeeping) has minimized these upsets.

In our laboratories we studied the effect of the various sewer discharges on clarification, and the data developed in these studies are discussed in detail in Section VII.

TABLE 37. CLARIFIER STUDY — COMBINED LOCKS PAPER CORPORATION
AVERAGE EFFLUENT QUALITY AND REMOVAL
VALUES FOR IPC AND MILL CLARIFIERS

	Effluent quality				Removal, %[a]		
	Suspended solids,	BOD$_5$			BOD$_5$		
Clarifier	mg/l	Total, mg/l	Soluble, mg/l	Color units	Total	Soluble	Color
A. Both units without chemical flocculating agents:							
IPC	46	232	190	205	22.1	8.6	-20.6
Mill	48	254	188	227	13.3	8.3	-33.5
B. IPC unit with ferric chloride (75 mg/l Fe^{3+}), and mill using no chemical treatment:							
IPC	45	169	147	112	40.1	25.8	32.5
Mill	74	214	187	207	24.1	5.6	-24.7
C. IPC unit with ferric chloride (75 mg/l Fe^{3+}) + Nalco 73C32 (0.75 mg/l), and mill using no chemical treatment:							
IPC	66	196	168	92	34.4	20.4	31.8
Mill	46	214	209	199	28.4	1.0	-47.4
D. IPC unit with ferric sulfate (100 mg/l Fe^{3+}), and mill using no chemical treatment:							
IPC	37	136	129	77	41.9	25.4	18.1
Mill	50	166	152	130	29.0	12.1	-38.3
E. IPC unit with alum (300 mg/l), and mill using no chemical treatment:							
IPC	60	205	197	123	32.6	13.2	31.7
Mill	54	240	216	241	21.0	4.8	-33.9
F. IPC unit with alum (300 mg/l) + Hercofloc 812.3 (0.75 mg/l), and mill using no chemical treatment:							
IPC	85	237	208	129	50.9	13.3	30.3
Mill	56	262	212	229	30.9	11.7	-23.8
G. Both units without chemical flocculating agents (gravity sedimentation only):							
IPC	50	239	214	252	27.8	-1.4	-26.6
Mill	52	236	208	254	28.7	1.4	-27.6

---

[a] Mill did not sample influent; values are based on average of IPC influent.

SECTION VII

JAR TESTS WITH INDIVIDUAL SEWER DISCHARGES

GENERAL

In Section V of this report, the BOD_5 sources making up the total discharge of the mill to the clarifier were listed and briefly discussed. In the field studies (Section VI) we had noted a marked decrease in the efficiencies of both the mill and IPC clarifiers when larger than usual amounts of spent liquor were in the waste stream being processed.

In this section we detail and discuss the studies made on the efficiency of the soluble BOD_5 removals realized when individual sewer streams were treated. These individual sewer effluents were also used to make a "synthetic" mill effluent by compositing each on the basis of its volume to the overall volume of the total mill discharge.

Using these same individual streams, we prepared various composites, omitting one stream at a time, to determine the effect the omission had on the overall efficiency of BOD_5 removal by clarification.

Ferric chloride (25, 50, 75, 100, and 150 mg/l Fe^{3+}), alum (50, 100, 150, 200, 250, and 300 mg/l) and combinations of these two primaries with 0.75 mg/l of either Hercofloc 812.3 or Nalco 73C32 were used with each stream and composite.

Values for total BOD_5 and, when time permitted, soluble BOD_5 for the treated samples were compared with untreated (settled) control samples for the determination of BOD_5 removal.

TESTS ON MOSINEE INDIVIDUAL SEWER SAMPLES

Some of the mill discharge streams, especially the "high density," pulp mill and paper machine sewers, could be effectively treated with the proper concentration of the primary flocculants (Figures 11 and 12, Legends 1-11) or primary flocculant-polymer combinations (Legends 12-23). These bar graphs display that in others, such as the foul evaporator condensate, soda recovery wastes, and digester room wastes, the BOD_5 level was not substantially affected by any of the flocculating agents. Those bars shown below the zero line in the lower section of the figures indicate negative removal of BOD, probably due to prolonged holding time. These waste flows should be treated by routes other than clarification (i.e., steam stripping of the condensates).

In our earlier work with the individual streams we found that toxic materials were in some samples, and they interferred with the BOD_5 test (Table 38). Therefore, we could not make even good estimates of the concentration

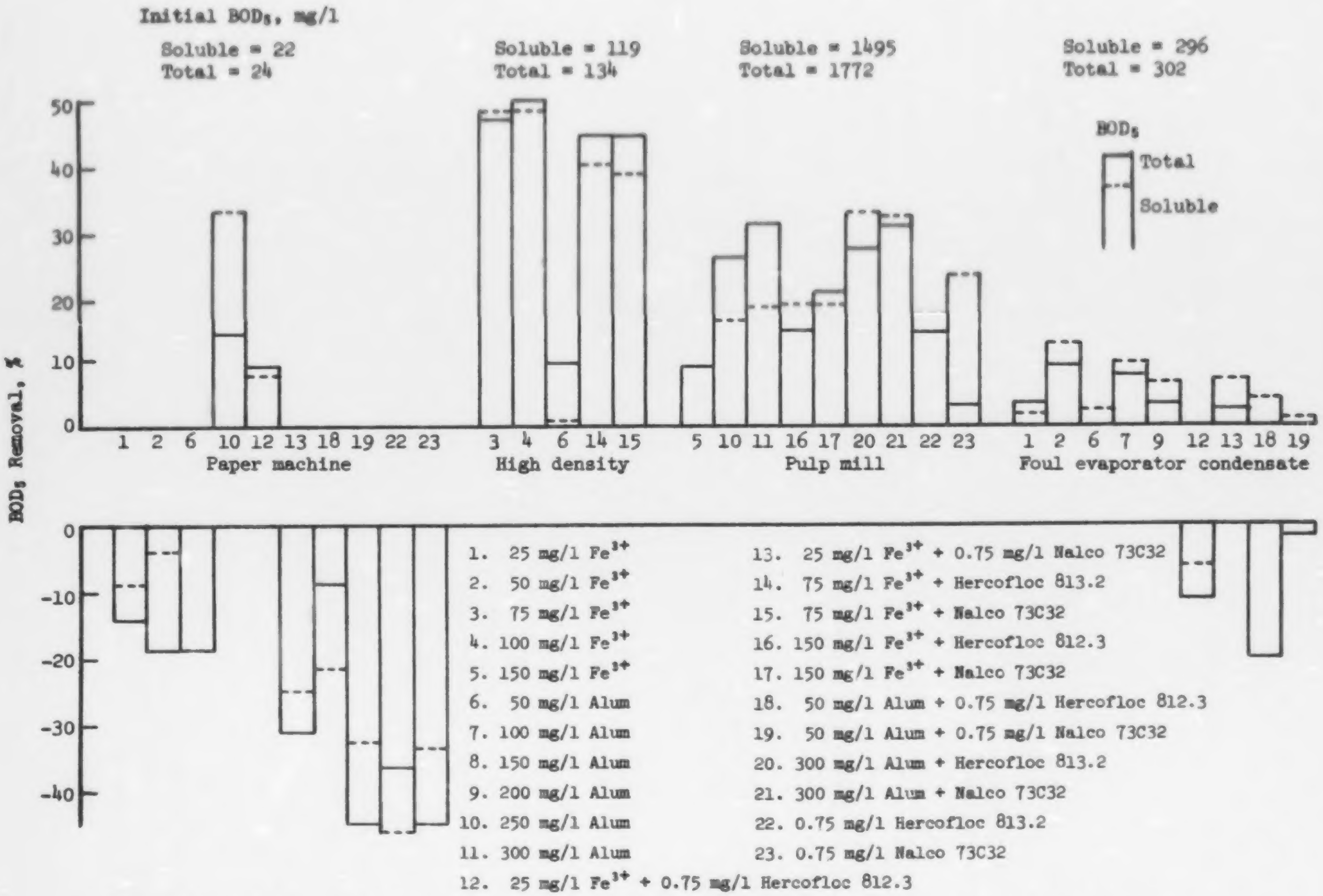


Figure 11. Jar tests on wastes from individual sewers in the Mosinee mill (paper machine, high density, pulp mill, and foul evaporator condensate).

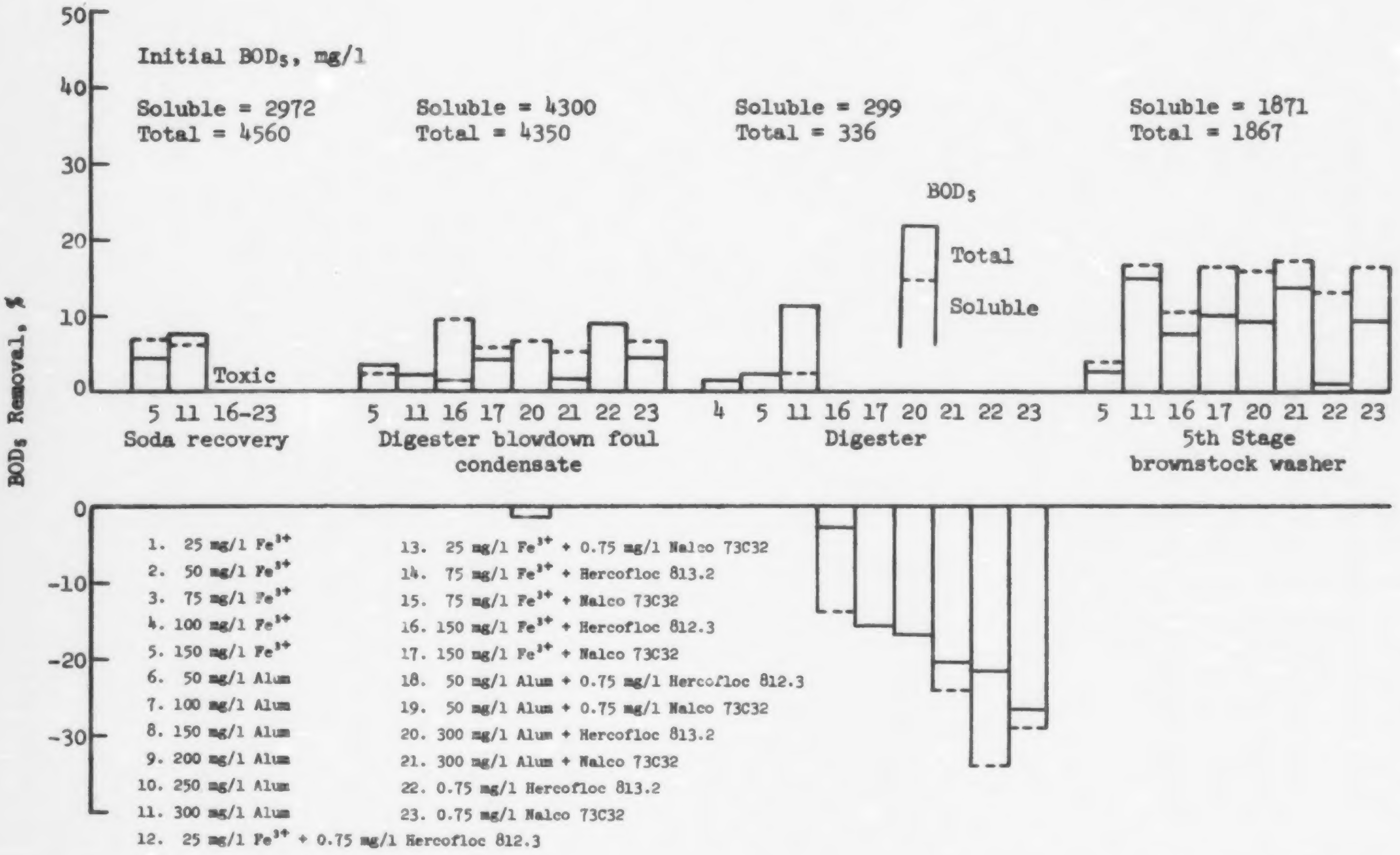


Figure 12. Jar tests on wastes from individual sewers in the Mosinee mill (continued) (soda recovery, digester blowdown, foul condensate, digester, and 5th stage brownstock water).

TABLE 38. BOD OF INDIVIDUAL EFFLUENT STREAMS AND TOTAL MILL EFFLUENT OF MOSINEE MILL

Source	Dilution	mg/l
Digester sewer	120	637
	600	633
Pulp mill sewer	150	1210
	300	1490
	600	1629
	1500	1620
5th Stage brownstock washer	300	940
	600	1089
	1000	1353
	2000	1340
High density sewer	30	141
	100	174
	150	172
Foul evaporator condensate	120	570
	300	762
	600	751
Digester blowdown foul condensate	300	1023
	600	1325
	750	1300
Soda recovery sewer	600	4236
	1500	4188
Total mill effluent	60	271
	150	280

of BOD_5 in these streams without careful dilution techniques. Excessive amounts of these same toxic agents would also interfere with the operation of a biological secondary treatment system and for this reason, if for none other, their presence in the total effluent should be held to a minimum or completely eliminated. Discharges into individual mill sewers were used to prepare a "synthetic" total mill effluent in the following volume relationships:

	Million gal/day	% of Total
Paper machine	10	77.9
High density	1.5	11.7
Pulp mill	0.6	4.6
Foul evaporator condensate	0.3	2.3
Soda recovery	0.28	2.2

Digester blowdown	0.07	0.6
Digester	0.05	0.4
5th Stage brownstock washer	0.035	0.3
Total	12.835	100.0

To find the conditions for maximal BOD_5 reduction when individual wastes were omitted from the system, we made combinations of seven of these eight wastes and treated them also in jar tests. Data in Figure 13 indicate that higher levels of BOD_5 removal could be achieved with less chemical if certain individual discharges were eliminated from the flow. That is:

1. The "total" effluent required 250 mg/l of alum for 17 percent reduction or 75 mg/l Fe^{3+} for 42 percent reduction in BOD_5.
2. With the soda recovery sewer flow eliminated, a 250 mg/l alum level resulted in 26 percent reduction and the Fe^{3+} at 50 mg/l resulted in a 51 percent removal of BOD_5.
3. The absence of the pulp mill sewer from the total flow, with all other flows present, permitted a 60 and 63 percent reduction in the BOD_5 concentration in the waste stream for 100 mg/l alum and 50 mg/l Fe^{3+}, respectively.

When 1 percent v/v of the digester room waste was added to a mixture of wastes having relatively good clarification characteristics (paper machine and high density wastes), higher concentrations of flocculating agent were needed to produce an effluent of adequate discharge quality (Figure 14).

Attempts to calculate BOD_5 balances for these various discharge combinations, and to correlate these with the actual BOD_5 values obtained, was apparently hindered by some interaction(s) between these wastes. This could have been due to changes in the toxicity of the mixtures for the microorganisms in the BOD_5 test.

The difficulty in calculating material balances for the total or soluble BOD_5 of the individual streams and composites is due to the fact that all of the initial BOD_5 values for these samples were on "settled" jar samples. Settling removes BOD_5 and the removed BOD could not be accounted for in the calculations of BOD_5 balances. In these samples, the interaction of the adsorbing character of fibers and particles with the dispersing character of the various mixtures could markedly affect BOD_5 removal during the settling step, thereby modifying the "initial" BOD_5 of the mixture. The importance of this interaction in the overall flocculation-clarification process should be investigated further in any attempt to improve the process.

TESTS ON INDIVIDUAL STREAMS FROM COMBINED LOCKS MILL

The five streams making up the bulk of the flow to the clarifiers at Combined Locks — from the main, "CM," wet room, Number 5 and Number 6 sewers — were tested individually for the removal of BOD_5 in jar tests with ferric chloride, alum and combinations of these with either Hercofloc 812.3 or Nalco 73C32. We also prepared a composite "total" mill effluent and composites lacking individual sewer outfalls, as we did with the Mosinee wastes.

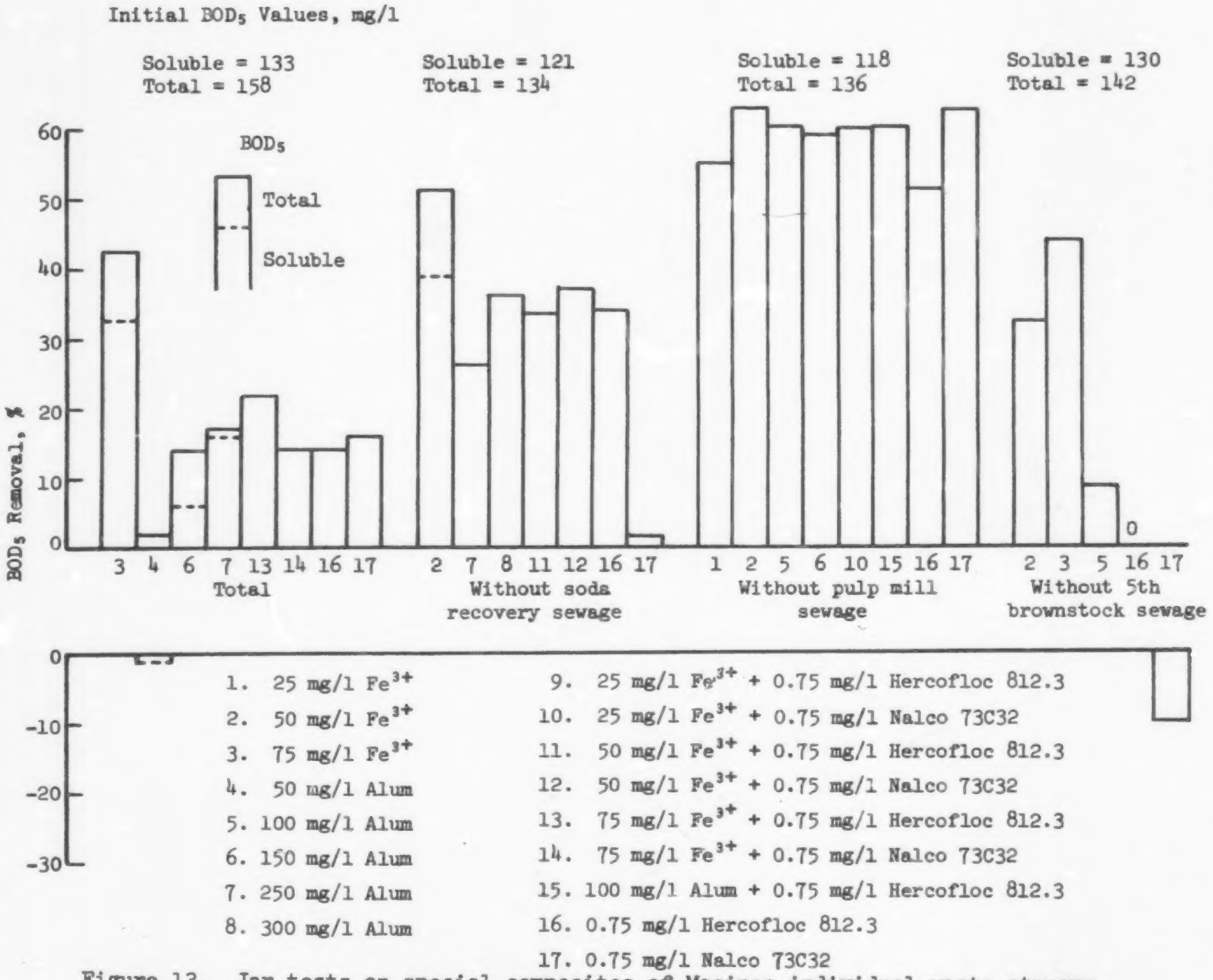


Figure 13. Jar tests on special composites of Mosinee individual waste streams.

As predicted by our earlier work, those streams having low spent liquor content, i.e., Number 5 and main sewers, had good supernatant quality (Figure 15). The BOD_5 removal was good with relatively low concentrations of Fe^{3+} or alum (Figure 16).

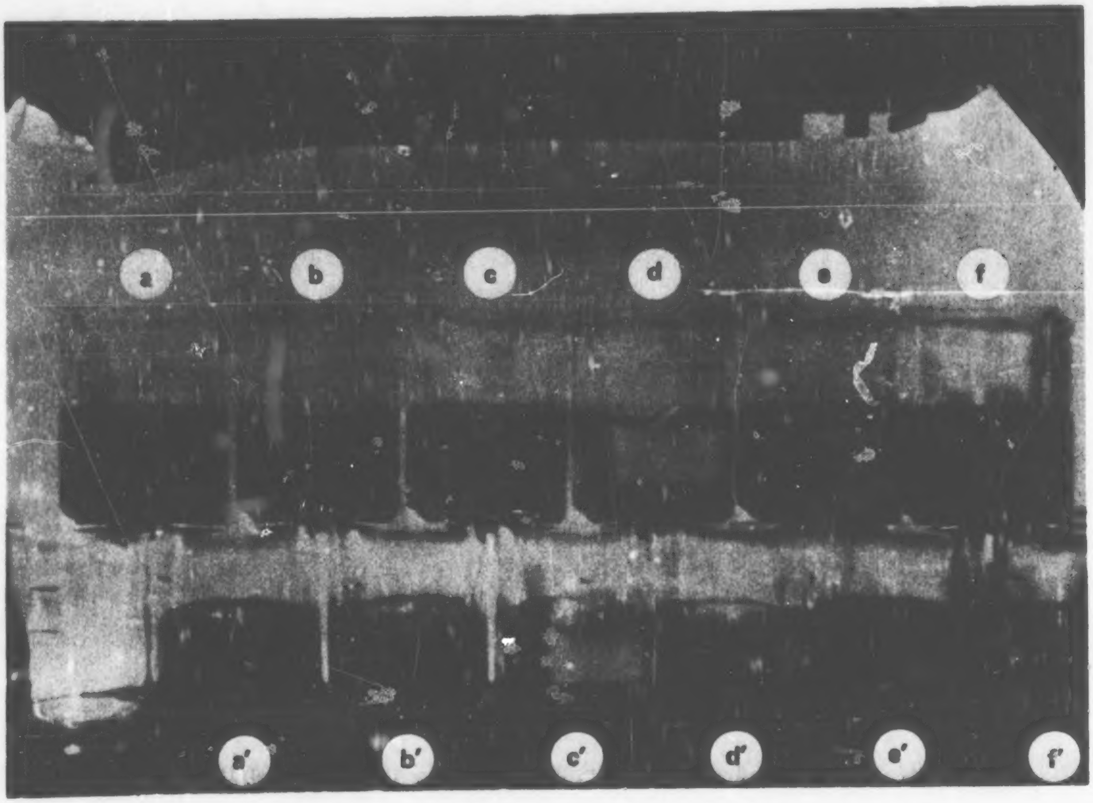


Figure 14. Jar tests show mixed effluents with addition of, left to right, 25, 50, 75, 100, and 150 mg/l Fe^{3+}; the control, no addition, is jar f. A Mosinee effluent was used composed of: (bottom row) paper machine and high density sewer effluent, and (top row) the above with 1 percent v/v digester room effluent.

The chemical concentrations of ferric chloride and alum required to effectively remove both suspended solids (for high supernatant clarity) and BOD_5 was higher for the "total" effluent than for the various composite streams (Figure 17). As the individual streams were removed from the system, the quantity of flocculants was reduced, especially for those mixtures without the "CM," wet room or Number 6 sewers. The Number 5 sewer stream had good removal characteristics, with low chemical requirements, as an individual stream, and omitting it from the mixture did not appear to enhance the BOD_5 removal.

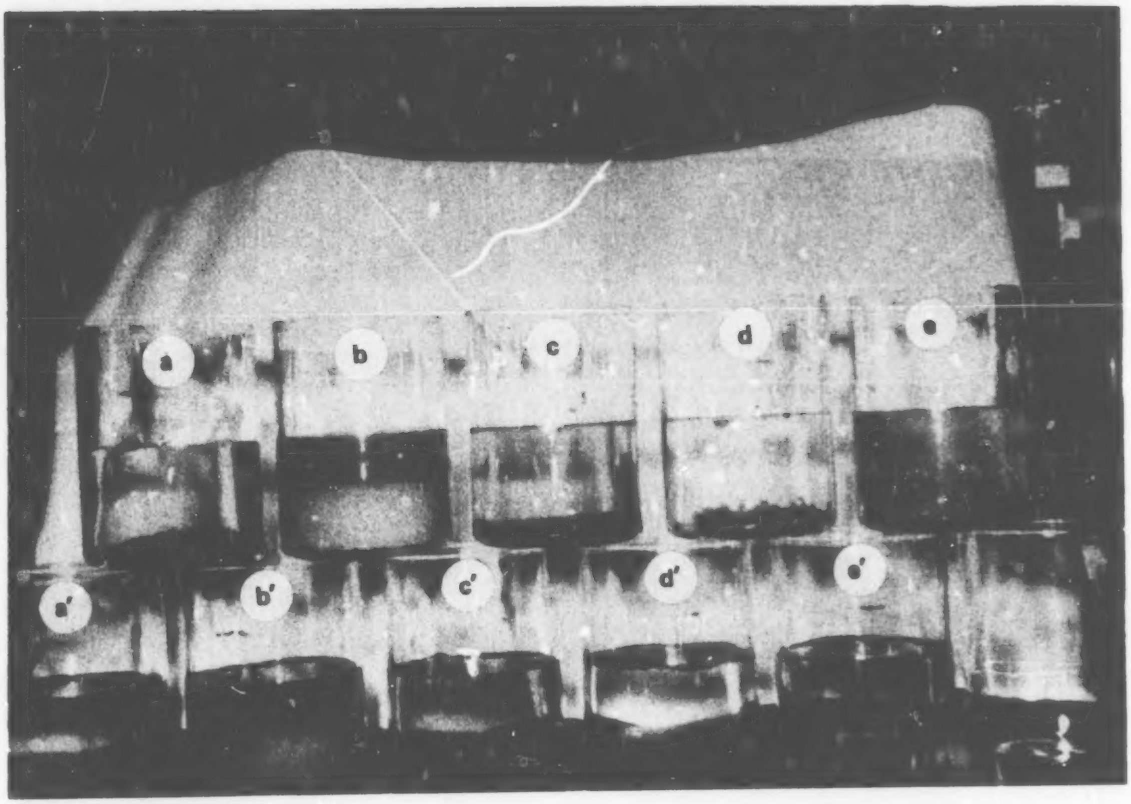


Figure 15. Jar tests with Combined Locks individual sewer effluents, a–e (main, "CM," wet room, machine No. 5 and machine No. 6). Top row: with 25 mg/l Fe^{3+}; bottom row: with 20 mg/l alum. Control wastes did not settle without additives and are not shown.

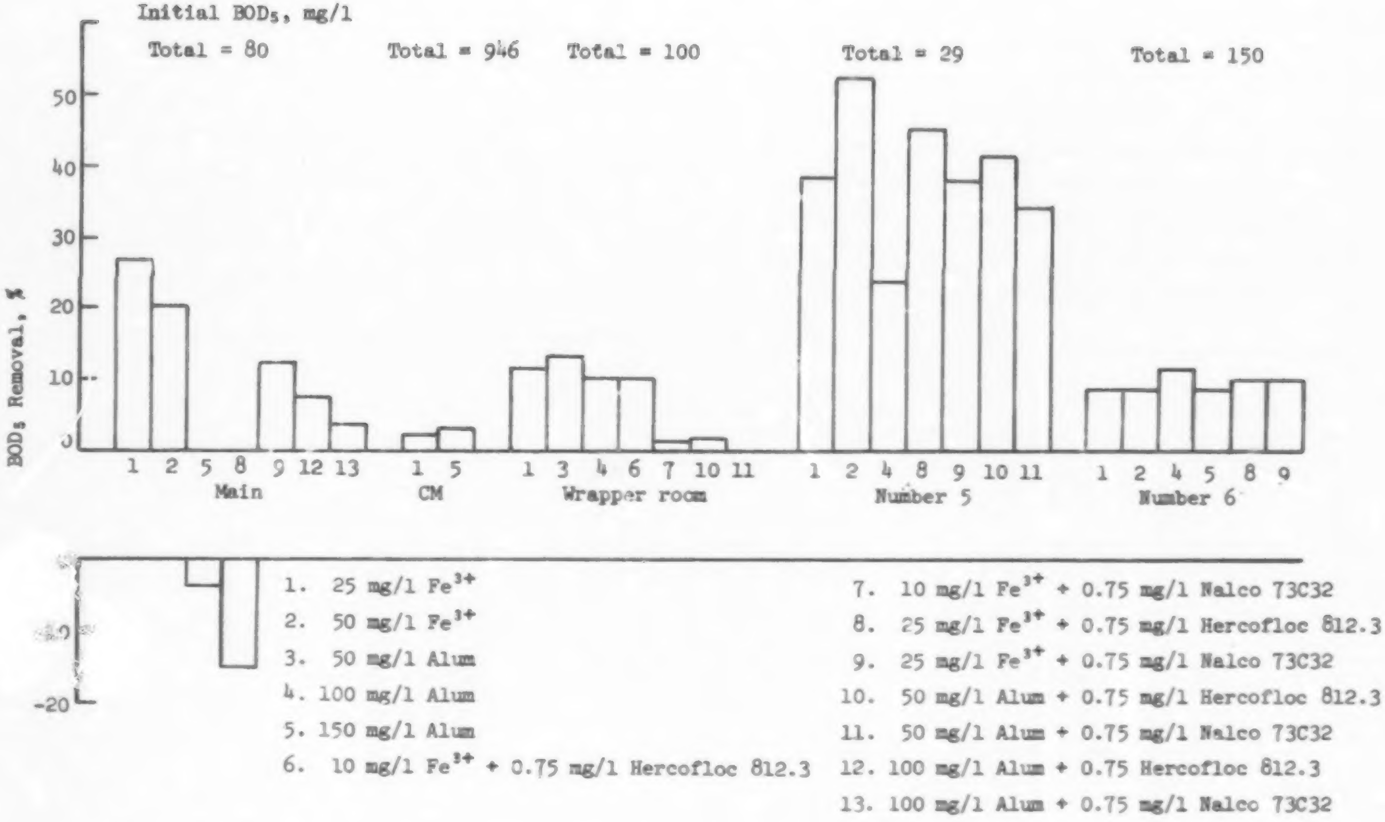


Figure 16. Jar tests on wastes from individual sewers in the Combined Locks mill.

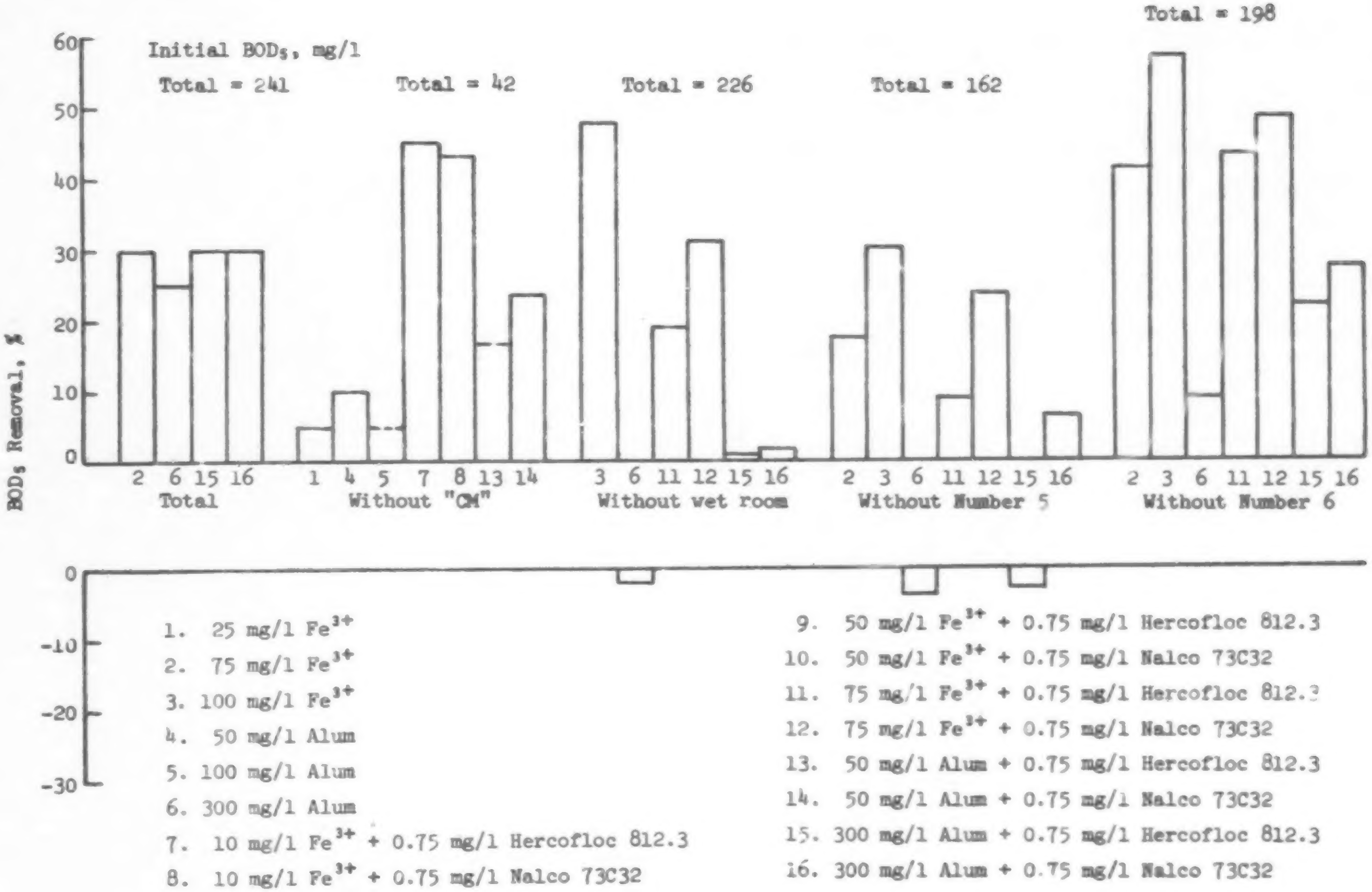


Figure 17. Jar tests on special composites of Combined Locks individual waste streams.

SECTION VIII

DISCUSSION OF THE MECHANISMS OF SOLUBLE BOD_5 REMOVAL

The studies with jar and pilot-scale clarifiers have readily confirmed that substantial quantities (as much as 20 to 50 percent) of the soluble BOD_5 are removed in clarifiers by coagulation aids and that the removal can be a significant factor in the treatment of pulp and paper mill waste waters.

Our data show that, at least to some extent, the reactions leading to improved BOD_5 removal can be optimized in well operated and controlled clarifier systems. Several studies were made in an attempt to better define the mechanism for reduction of soluble BOD_5 during the treatment of process waters in primary clarifiers.

It had been evident from the beginning of the study that some of the soluble BOD_5 could be removed from the waste stream by several processes (membrane, ion-exchange) and that no one mechanism could be credited for the entire effect.

GEL CHROMATOGRAPHY STUDIES

The components responsible for the soluble BOD_5 in clarifiers can be divided into two classes, wood-derived chemicals and additives. The wood derived chemicals include degraded cellulose, hemicellulose, hemicellulose degradation products (reducing sugars, acetic acid, methanol and uronic acids), extractives and in small, perhaps minor amounts, metabolites common to living tissues (adipic acid, oxalacetic acid, etc.). Additives used in papermaking include starches, polysaccharides, gums, latexes, resins, dyes, etc. Some mills will also have organic solvents such as methanol, acetone, etc., which are biodegradable. The organic solutes that pass the 0.45-µm filter probably comprise colloids, low molecular weight polymers, oligomers, monomers and simple organic compounds.

To better understand the removal of soluble BOD_5 by coagulation, we treated the effluent from a chemimechanical mill (Combined Locks mill) with the various flocculating agents. Using gel chromatography we measured molecular size distribution before and after flocculation and clarification.

Samples were filtered on a 0.45-µm filter prior to chromatography. The gel chromatography was carried out on Sephadex G-50, a gel which excludes (allows no equilibration with the gel pores) molecular weights 10,000 and above and includes (allows complete equilibration with the gel pores) molecular weights of 500 and below. Molecular weights between 500 and 10,000 are fractionated according to the number of pores with which the molecules equilibrate.

Figure 18 shows the TOC (total organic carbon) of 2 ml of a tenfold concentrate as it elutes from a 1 x 55-cm column. The second curve shows that after flocculation with 70 mg/l ferric chloride not only are large molecular weight residues removed, but also low molecular weight molecules. The curves in Figure 19 were obtained when a similar sample (1-ml sample of fivefold concentrate) was fractionated on Sephadex LH 20 (mol. wt. 5000 to 200) before and after coagulating with 10 mg/l of Nalco 73C32, a cationic polyelectrolyte and analyzed for aldoses by the phenol-sulfuric acid test (8). The low molecular weight peak almost disappeared.

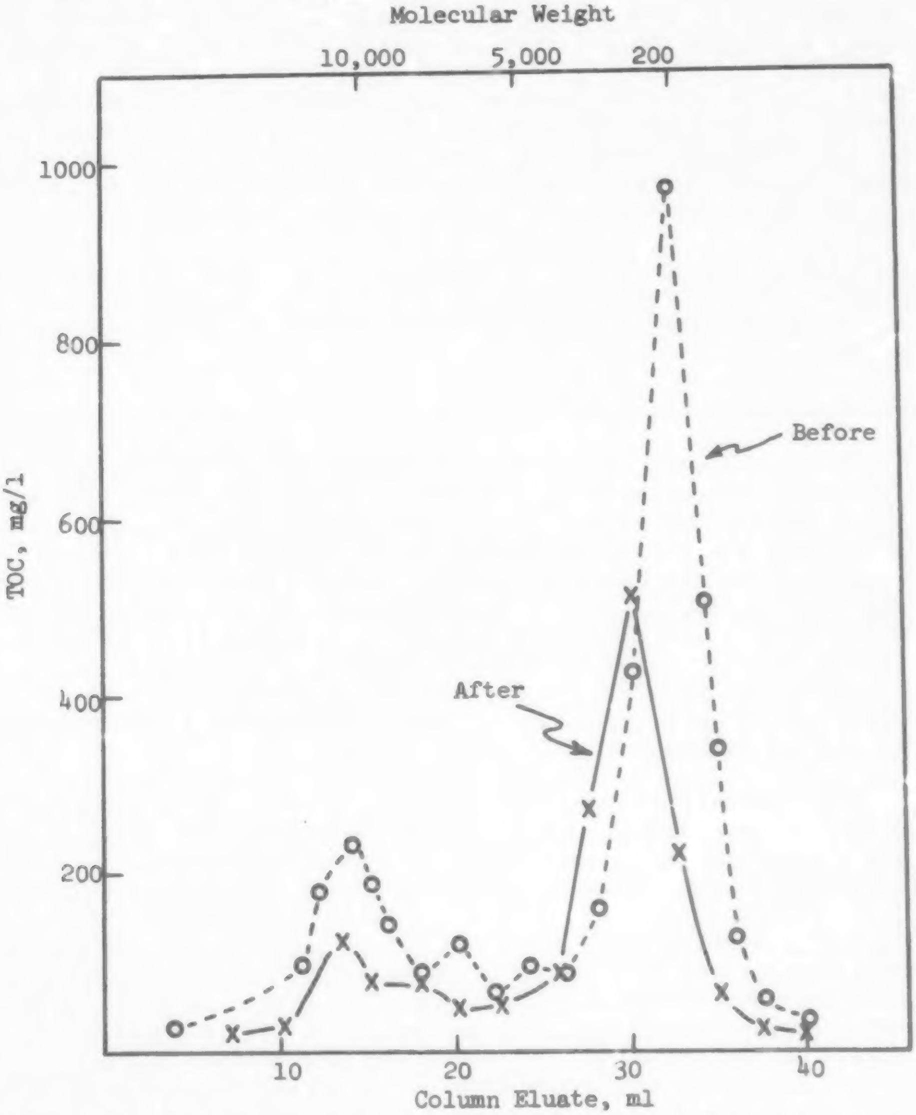


Figure 18. TOC and molecular weight distribution of gel-chromatographed chemimechanical mill effluent before and after coagulation with 70 mg/l Fe^{3+} as ferric chloride.

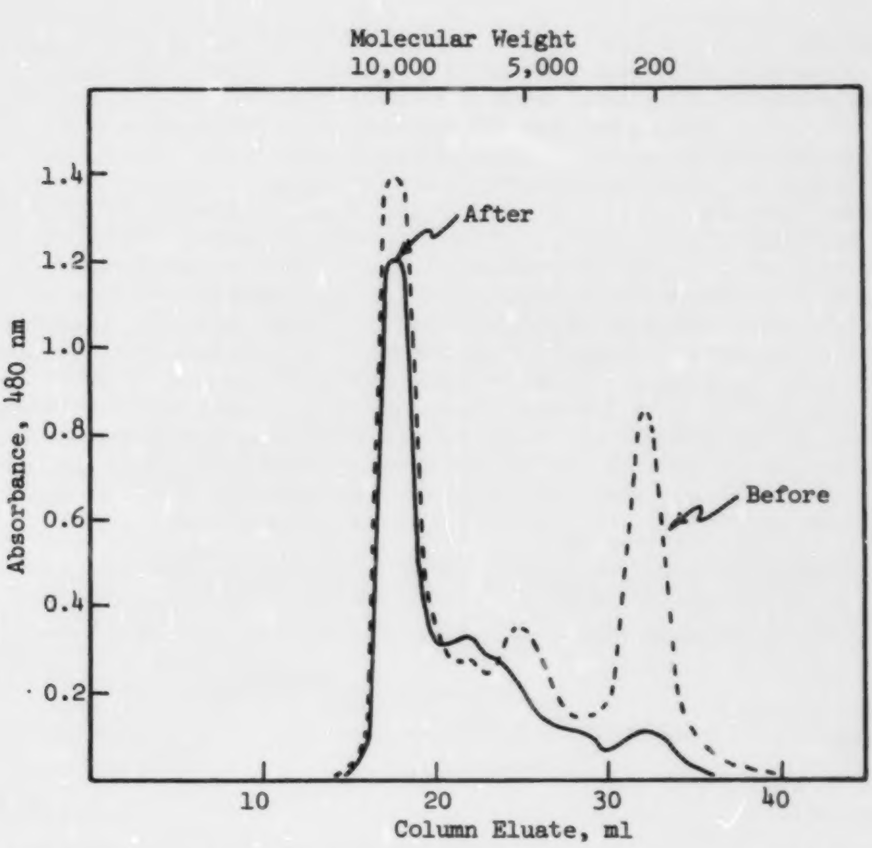


Figure 19. Phenol sulfuric acid test for aldoses and molecular weight determination of gel-chromatographed chemi-mechanical mill effluent before and after coagulation with 10 mg/l Nalco 73C32. One-ml samples of eluate were analyzed.

The phenol-sulfuric acid test measures aldoses and polymers of aldoses when borate interference is observed. The solutions analyzed in this report showed enough borate sensitivity to indicate the test was responding primarily to aldoses and polymers of aldoses and not to noncarbohydrate aldehydes.

When a sample fractionated on Sephadex G-50 was divided into three fractions corresponding to high, medium and low molecular weights and analyzed for TOC, aldose and BOD_5, the results summarized in Table 39 were obtained. The percentage change for the soluble BOD_5 was not as great as that observed for the aldoses or TOC. Apparently not only low molecular weight biodegradable materials were removed but also low molecular weight nonbiodegradable organics.

Das and Lomas explored the different mechanisms of the flocculation of cellulose fines with the cationic polymer polyethylenimine (2). They were able to show that bridging (the adsorption of two sections of a polymer to two colloids) was a significant part of the cellulose fines flocculation. Such a mechanism could also occur with the other polyelectrolytes and with ferric chloride which hydrolyzes and polymerizes to a polyelectrolyte (14). The mechanisms for the coagulation of cellulose fines involved collapse of their double layer followed by adsorption and bridging. Lower molecular weight residues were generally difficultly adsorbed. Their participation in coagulation probably depends on salt formation and chelation. Such salt formation by hydrolyzed iron can be demonstrated with gel chromatography. Figure 20 shows the elution curve for a mixture of ferrous ammonium sulfate and sodium gluconate. The complexes absorb ultraviolet light and are, therefore, detectable with the UV absorptiometer at 280 nm. Iron values were obtained by the o-phenanthroline test. Because the curve shows that at a pH of 2.0, most of the iron elutes from Sephadex LH-20 and G-15 (fractionation range 150 to 10,000) in the highest molecular weight fraction, the complexes probably have molecular weights of 10,000 and above. Figure 21 shows the distribution of the complexes when the pH of the solution was 7.0. At higher pH more of the iron was in the lower molecular weight fractions.

TABLE 39. REMOVAL OF DIFFERENT MOLECULAR WEIGHT FRACTIONS OF ORGANIC RESIDUES BY FLOCCULATION

	Sample[a]			
Effluent treatment	UNF	HMW	MMW	LMW
Phenol-sulfuric acid test; total absorbance, 480 nm				
Filtered	--	7.5	3.9	5.2
Flocced[b] and filtered	--	3.0	2.4	2.5
Reduction, %	--	59.9	38.6	51.9
TOC, mg/l				
Filtered	3424	774	457	2301
Flocced[b] and filtered	2150	320	272	1387
Reduction, %	43.9	58.6	40.5	39.7
BOD_5, mg/l				
Filtered	3840	552	487	2689
Flocced[b] and filtered	3080	379	368	2131
Reduction, %	19.8	31.3	24.4	20.7

[a] UNF, unfractionated; HMW, high molecular weight (10,000 and above); MMW, middle molecular weight (500-10,000); LMW, low molecular weight (500 and below).

[b] Flocced with ferric chloride, 70 mg/l Fe.

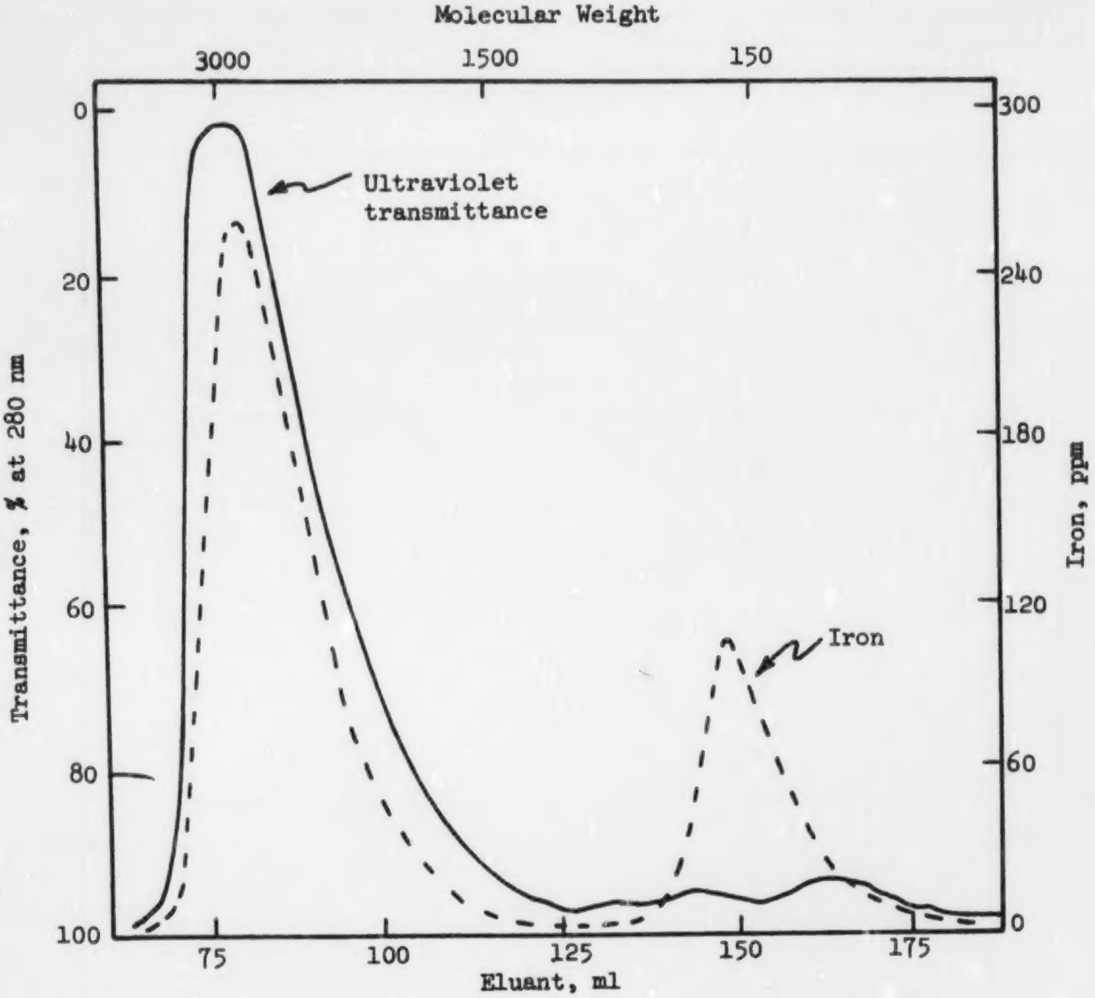


Figure 20. Ultraviolet light transmittance profile and molecular weight distribution of a gel-chromatographed solution of sodium gluconate and ferrous ammonium sulfate, pH 2.

If these biodegradable low molecular weight residues which participate in the coagulation are carboxylic acids, then the mechanism for their removal could be the complexing and/or chelating of the Fe^{3+} of the ferric chloride. As the ferric chloride hydrolyzes, more and more insoluble oligomeric forms of the hydroxide are formed. Whether or not the iron system would flocculate the low molecular weight residues without concomitant flocculation of polymers and/or suspended solids was not determined.

The types of carboxylic acids which might be derived from wood and form complexes with iron include the Krebs cycle acids (citric, adipic, oxalacetic, etc.), oxalic, aldonic, and uronic acids, and aromatic acids. Since little ultraviolet absorption was found associated with the low molecular weight gel chromatography fractions, aromatic residues have not been considered in this phase of the study.

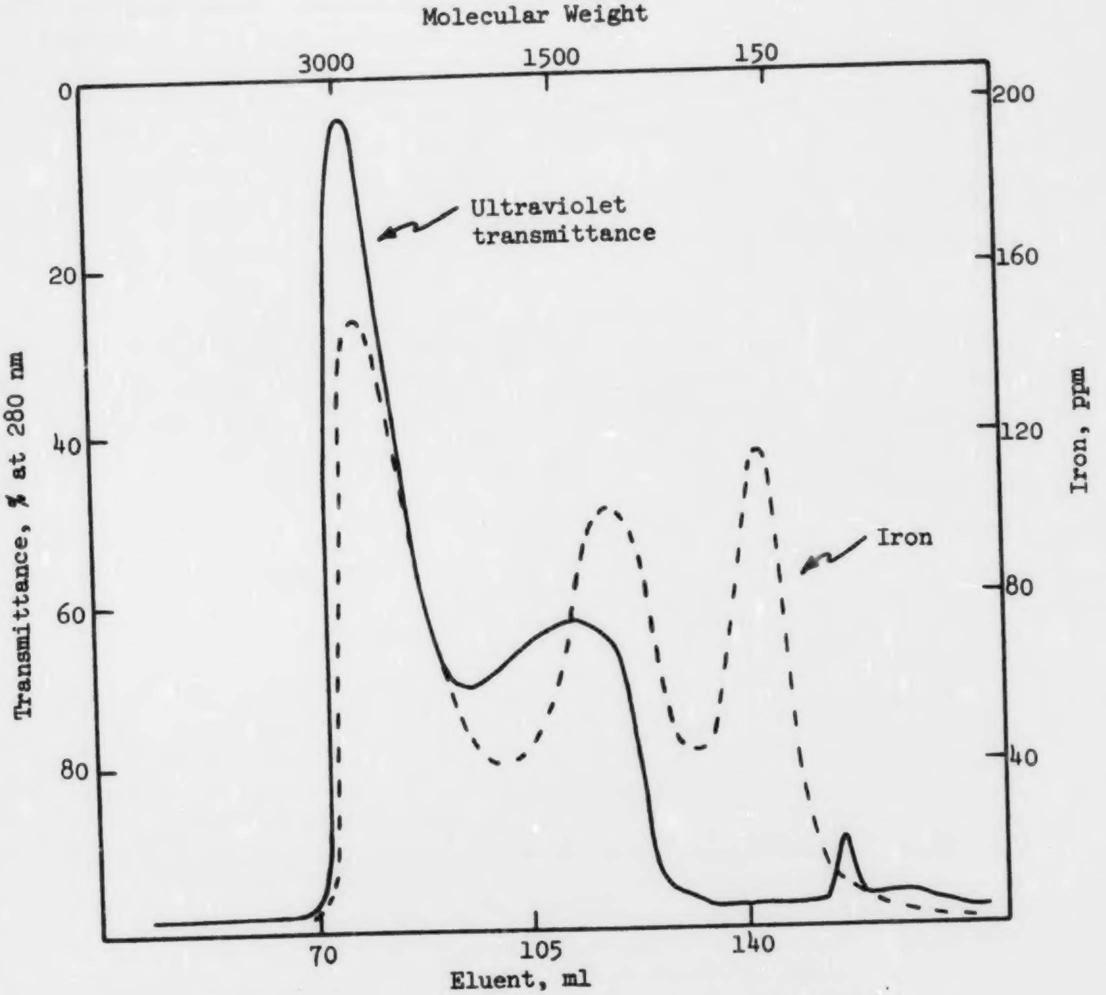


Figure 21. Transmittance and molecular weight distribution of a gel-chromatographed solution of sodium gluconate and ferrous ammonium sulfate, pH 7.0.

The sewer to the Combined Locks clarifier has five principal tributaries two of which gave aldose test responses strong enough for analysis by gel chromatography after the effluent was concentrated fivefold. The column elution curves are shown for the digester room effluent and the paper mill effluent (Figure 22). The digester room effluent showed predominantly high molecular weight residues and the paper mill effluent, low molecular weight residues.

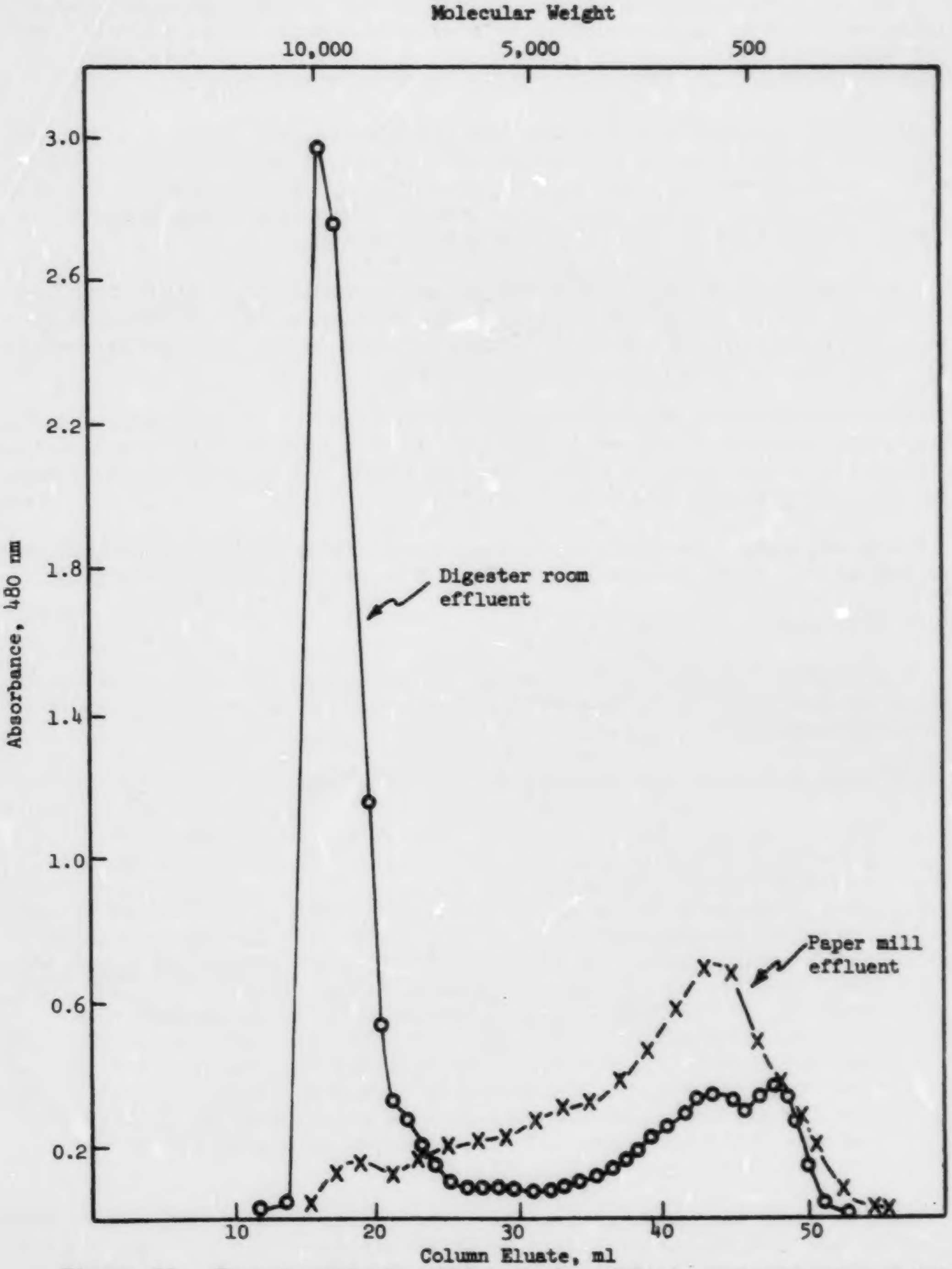


Figure 22. Phenol sulfuric acid test for aldoses and molecular weight distribution of gel-chromatographed chemimechanical pulp mill effluents.

Since this particular mill uses starch as one of its additives, one of the aldoses could be glucose and/or related starch degradation products.

STUDIES ON INFLUENT AND EFFLUENT SAMPLES FROM THE FIELD TRIALS

Clarifier influent and effluent samples from the two trials, at Mosinee and Combined Locks mills, were sent to the Analytical Section of the Institute for carbohydrate and weak acid determinations. Data are given in Table 40 for the results of these analyses on samples from high, intermediate and low soluble BOD_5 removal levels during clarification.

The carbohydrates were determined by gas chromatography after acid hydrolysis and derivative formation (15). The weak acids were determined by passing the sample through a cation-exchange resin column and conductimetrically titrating it with 0.1*N* sodium hydroxide.

No consistent correlation was apparent between the soluble BOD_5 and the carbohydrate removals, indicating that in the high soluble BOD_5 removals some precursor(s), in addition to other than the oligo- and polysaccharides, were being removed by flocculation and clarification.

There was slight correlation between the soluble BOD_5 and weak acid removal values for these samples, particularly those from the Mosinee study.

STUDIES WITH MODEL COMPOUNDS

On a modest scale we screened model organic compounds for removal from solution by flocculation in order to learn more about the chemical nature of susceptible compounds.

The compounds were selected on the following basis:

1. Those compounds having at least some structural relation to substances found in mill effluents, either as atypical compounds or "families of compounds" (16-18);
2. Those compounds with some BOD_5 without marked "toxic" effects; and
3. Compounds having sufficient solubility so that gas chromatography, total organic carbon or some other convenient analytical procedure could be used to monitor the results of jar tests.
4. Removals of TOC from pure solutions were early recognized to be critically affected by pH. This variable was evaluated carefully and the interesting and probably important results provided in the following figures are discussed with the realization that the highest levels of TOC removal were often noted at pH levels outside the ranges normal for mill wastes or discharged to treatment systems.

The jar tests were made with added fiber in the form of unbleached kraft pulp which had been disintegrated in an Oster blender for 5 minutes to provide a surface area for adsorptive bridging. Fibers had increased the removal of BOD_5 in some of our earlier work (Section V). This effect was confirmed with two runs with hydroxybenzoic acid and *p*-methylbenzoic acid with Fe^{3+}

TABLE 40. REMOVAL OF CARBOHYDRATES AND WEAK ACIDS FROM MOSINEE AND COMBINED LOCKS WASTE STREAMS BY PILOT-SCALE CLARIFICATION[a]

Total BOD_5, mg/l		Soluble BOD_5, mg/l		Carbohydrates, mg/l		Weak acids, meq/g[b]		Removal, %			
								BOD_5[c]		Carbo-hydrates	Weak acids
Influent	Effluent	Influent	Effluent	Influent	Effluent	Influent	Effluent	T	S		
Mosinee Samples											
158	83	117	78	8.0	4.2	4.7	0.12	48	33	48	97
160	90	136	90	9.0	5.6	2.1	0.16	44	34	43	92
148	122	108	92	5.7	8.7	4.6	3.0	18	15	-53	35
147	120	110	98	5.5	6.4	2.9	1.4	18	11	-16	52
150	136	112	108	15.8	4.8	1.8	1.8	9	4	70	0
94	92	79	76	4.8	9.4	2.9	1.2	2	4	-8	59
Combined Locks Samples											
226	114	107	82	10.5	18.4	3.1	1.7	50	23	-75	45
180	84	104	78	22.9	31.0	1.5	1.2	53	25	-35	20
386	239	234	216	46.8	62.2	3.2	2.3	38	8	-33	28
267	240	211	202	19.7	24.8	3.7	3.3	10	4	-26	11

[a] Samples were from high, medium, and low BOD_5 removal levels during clarification.

[b] Milliequivalents/gram of solids.

[c] T, total; S, soluble.

(as $FeCl_3$) at various pH's, with and without the addition of fibers (Figure 23). TOC analyses were used to monitor changes in chemical concentrations of the model compounds before and after clarification.

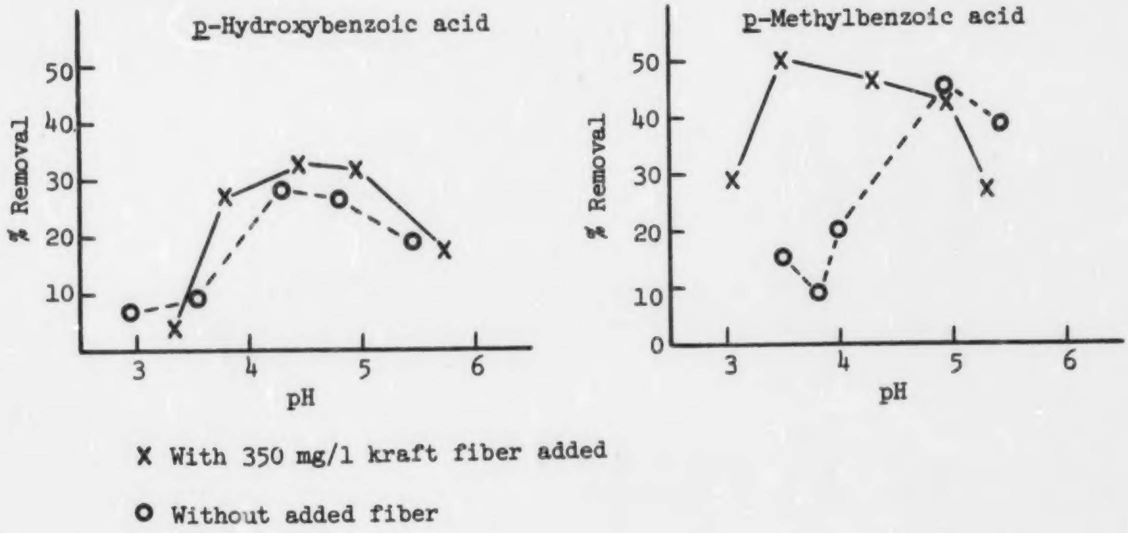


Figure 23. Effect of pulp fibers on removal of soluble compounds with 100 mg/l Fe^{3+} (as $Fe Cl_3$) at various pH's. ——, 350 mg/l kraft fiber added; ----, no fiber added.

Solutions were made from an amount of the model compound calculated to give a TOC level of 90-95 mg/l in the final volume to be used in the study. This was first dissolved in approximately 4 liters of distilled water; the correct amount of blended fiber was added (350 mg/l final volume), and the volume was brought to either seven or nineteen liters (final volume), depending upon whether one or two sets of jars were to be used for the evaluation.

One liter of the mixture containing the model compound and fibers was added to each of six jars. Five of the jars were treated with flocculating agent (various concentrations) and the sixth was used as an untreated "control." All jars were settled, sampled and filtered (0.45 µm). TOC was determined on the filtrates from the "control" and the five treated samples. All "removal" values are based on a comparison with the TOC concentration of the "control" after filtration. In this way the adsorption of the model compound on the fibers without flocculant addition could be monitored. In all tests the adsorption onto fibers of the controls was less than 8 percent (based on weight calculation), except for the arrowroot starch and dextrose which were found to be 65 and 24 percent, respectively.

Ferric chloride and alum were the primary flocculants used. Alum (Table 41) did not remove significant amounts of model compounds except polygalacturonic acid (87 percent removed at 200 mg/l alum concentration). The highest removal of model compounds obtained with lime up to 500 mg/l was 2 percent.

TABLE 41. TOC REMOVAL FROM SOLUTIONS OF MODEL COMPOUNDS TREATED IN JAR TESTS WITH ALUMINUM SULFATE[a]

Compounds	Removal of TOC, %
3,4-Dihydroxycinnamic acid	0.0[e]
Hydroxymalonic acid (tartronic acid)	1.0[e]
Methylmalonic acid	1.0[e]
D-Galacturonic acid	1.1[e]
p-Hydroxybenzoic acid	2.2[e]
Propanedioic acid (malonic acid)	2.6[e]
p-Methylbenzoic acid	3.2[e]
Dextrose	4.0[e]
Isopentyl alcohol (isoamyl alcohol)	4.7[b]
1,4-Butanedioic acid (succinic acid)	7.4[e]
4-Hydroxy-3-methoxycinnamic acid (ferrulic acid)	8.3[e]
3-Methoxy-4-hydroxy benzaldehyde (vanillin)	9.1[e]
trans-Butenedioic acid (fumaric acid)	10.1[e]
Arrowroot starch	11.4[d]
p-Hydroxycinnamic acid	13.3[c]
Benzylmalonic acid	34.4[e]
Polygalacturonic acid	87.0[d]

[a] All compounds were treated with all levels of alum. Only the best removals are listed in this table.
[b] Alum = 50 mg/l.
[c] Alum = 100 mg/l.
[d] Alum = 200 mg/l.
[e] Alum = 300 mg/l.

Data for the TOC removed when other compounds were similarly tested are given in Figure 24a-e. These data are very complex, with low molecular weight short-chained compounds (acetic acid, ethyl acetate) being removed at a 20 percent level, 2-pentanol and tertiary amyl alcohol showing less than 5 percent removal and hexanedioic acid, 40 percent removal. Several aromatic carboxylic acids had high removals, while galactouronic acid reductions were less than 5 percent (Figure 24e).

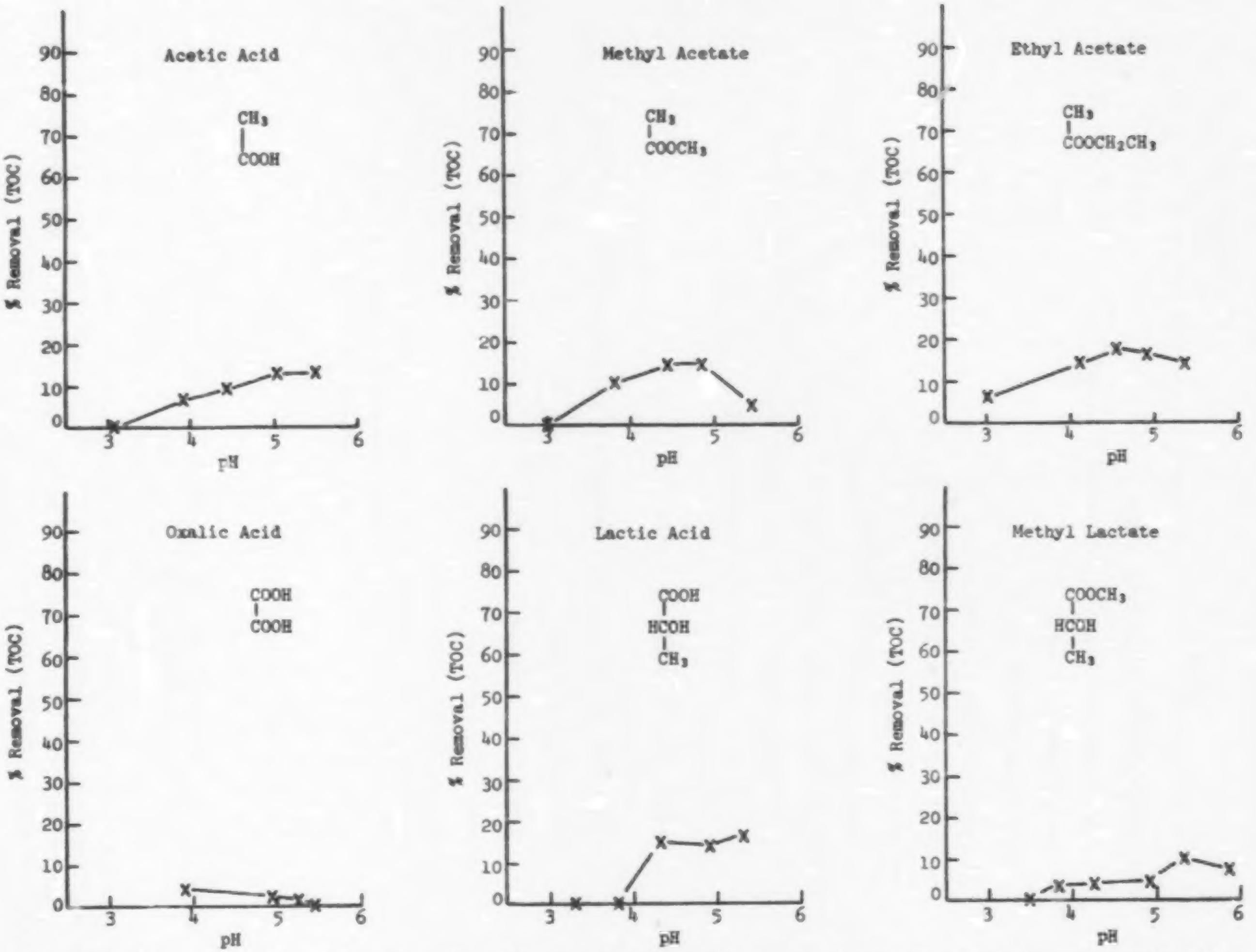


Figure 24a. Effect of kraft pulp fibers at 350 mg/1 on removal of soluble compounds with 100 mg/1 of Fe^{3+} (as $FeCl_3$) at various pH's (acetic acid, methyl acetate, ethyl acetate, oxalic acid, lactic acid, and methyl lactate).

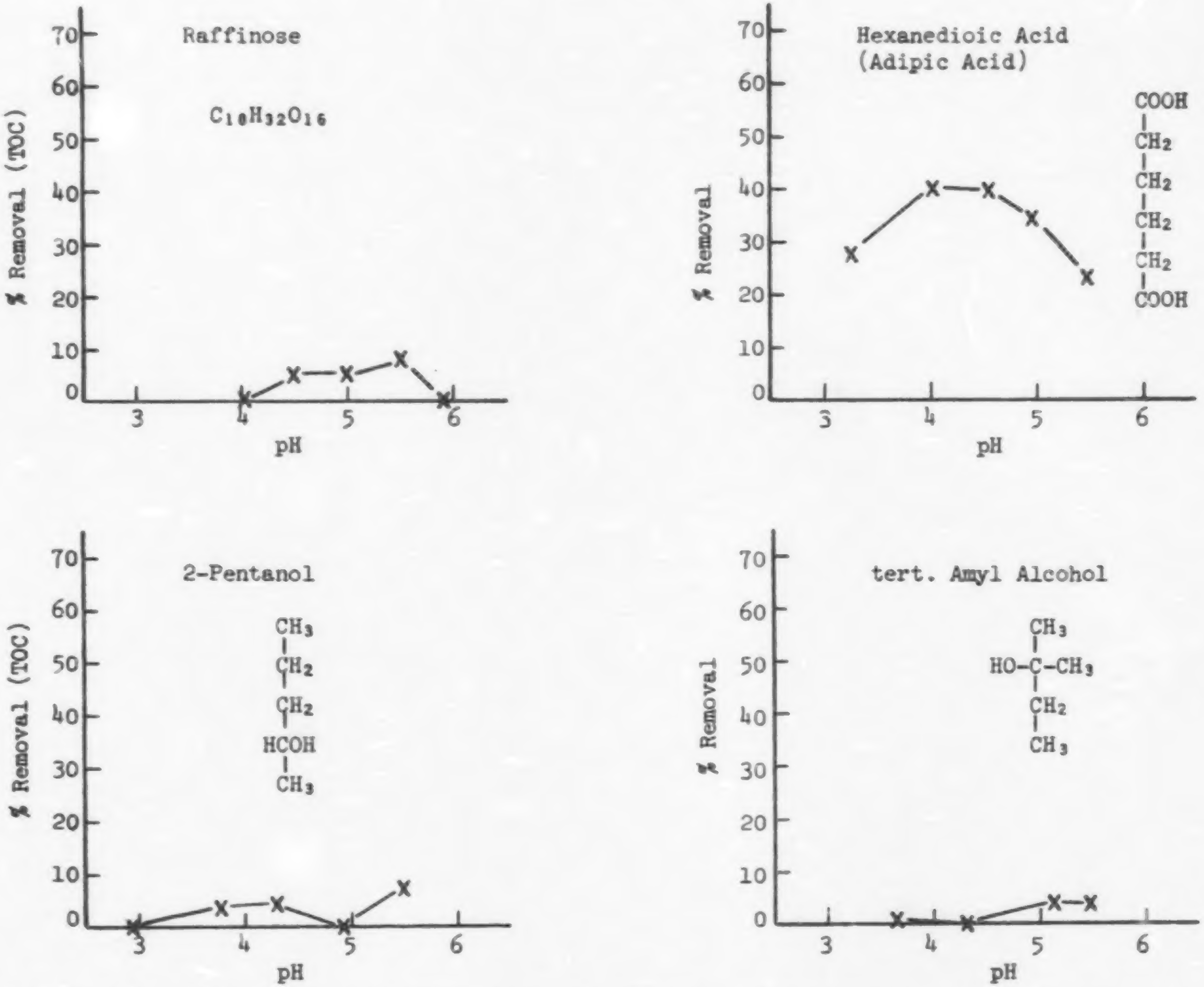


Figure 24b. Effect of kraft pulp fibers at 350 mg/l on removal of soluble compounds with 100 mg/l of Fe^{3+} (as $FeCl_3$) at various pH's (raffinose, hexanedioic acid, 2-pentanol, and tertiary amyl alcohol).

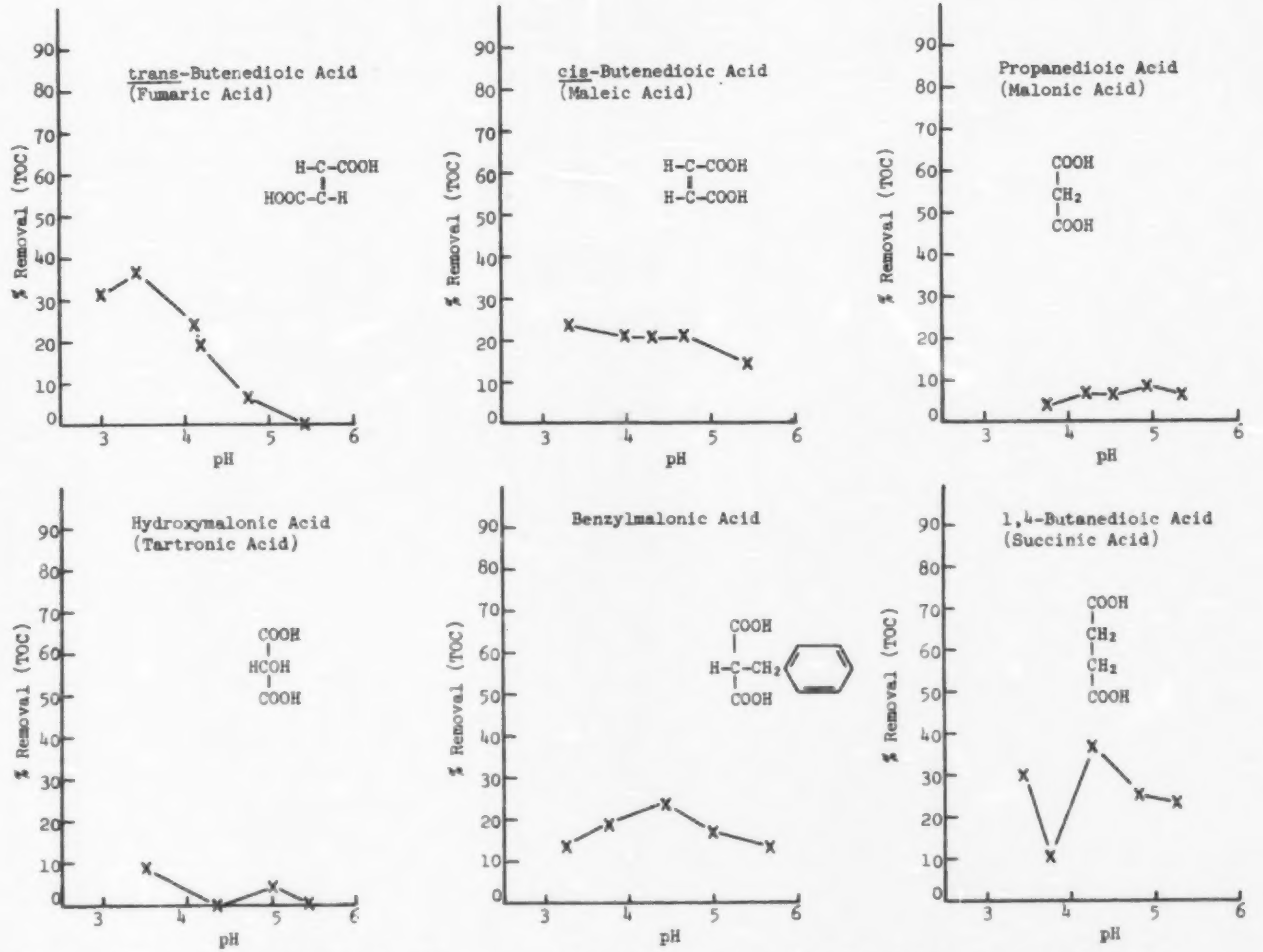


Figure 24c. Effect of kraft fibers at 350 mg/l on removal of soluble compounds with 100 mg/l of Fe^{3+} (as $FeCl_3$) at various pH's (*trans*-butenedioic acid, *cis*-butenedioic acid, propanedioic acid, hydroxymalonic acid, benzylmalonic acid, and 1,4-butanedioic acid).

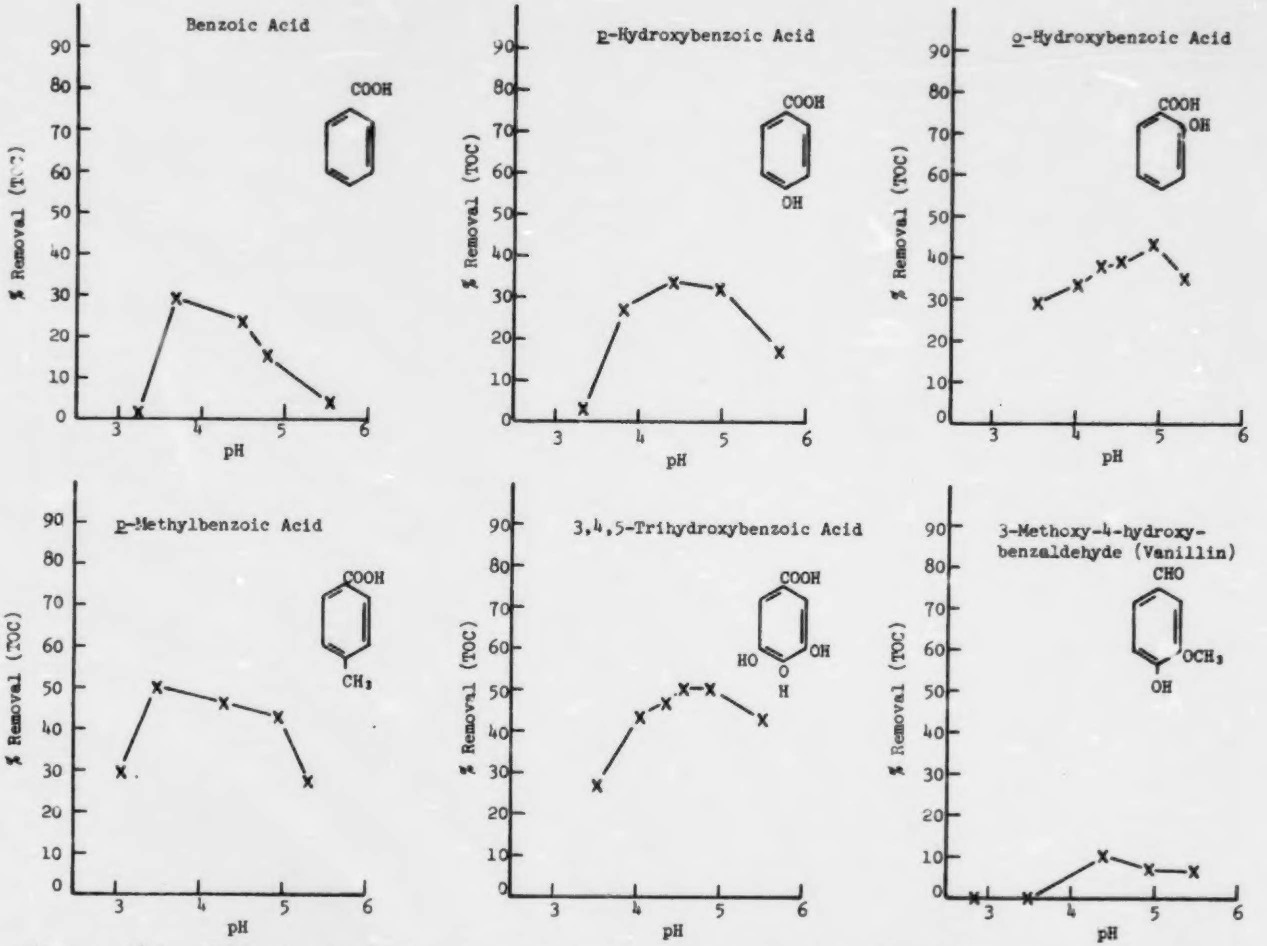


Figure 24d. Effect of kraft fibers at 350 mg/l on removal of soluble compounds with 100 mg/l of Fe^{3+} (as $FeCl_3$) at various pH's (benzoic acid, p-hydroxybenzoic acid, o-hydroxybenzoic acid, p-methylbenzoic acid, 3,4,5-trihydroxybenzoic acid, and 3-methoxy-4-hydroxy-benzaldehyde).

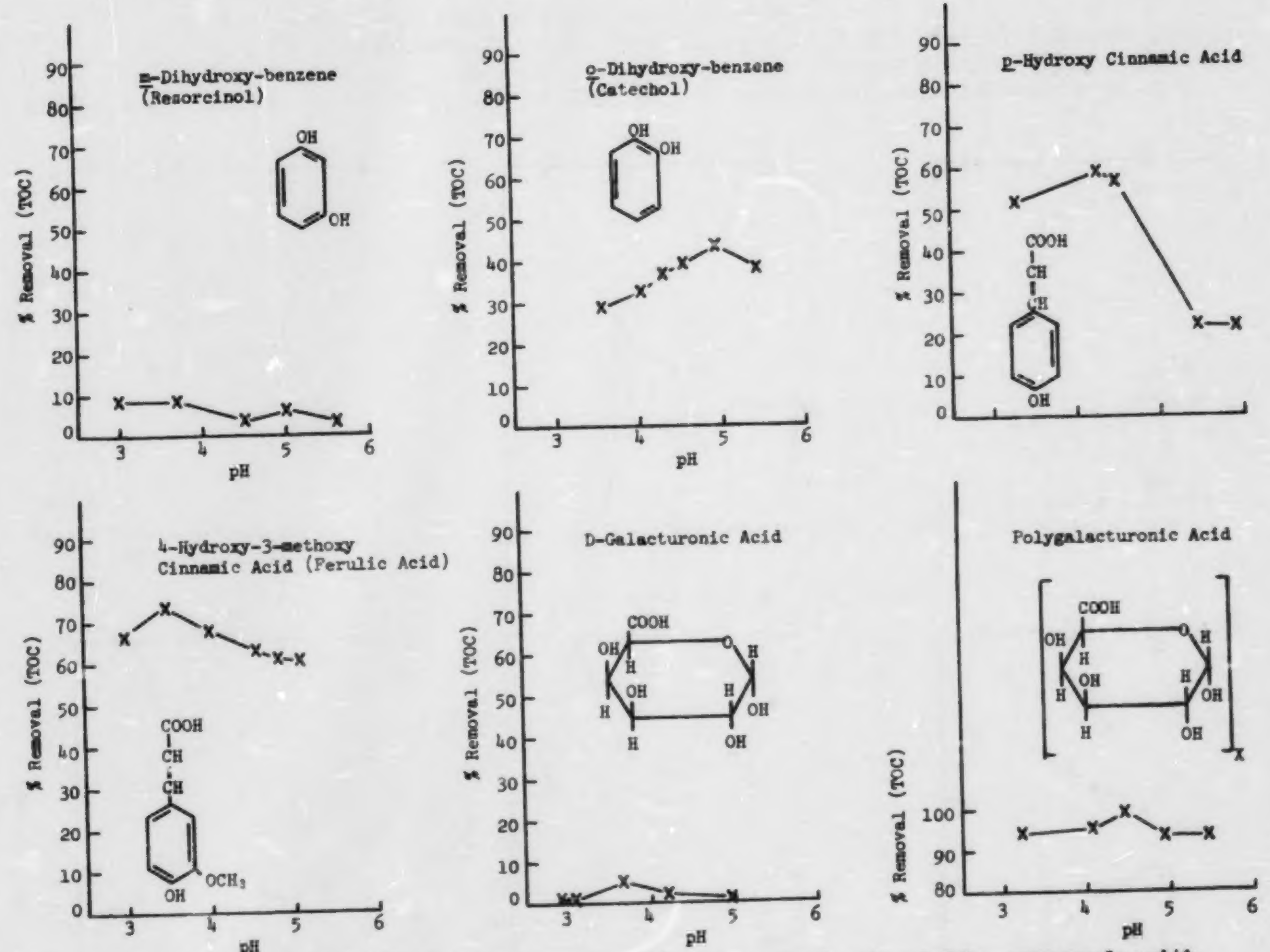


Figure 24e. Effect of kraft fibers at 350 mg/l on removal of soluble compounds with 100 mg/l of Fe^{3+} (as $FeCl_3$) at various pH's (m-dihydroxy-benzene, o-dihydroxy-benzene, p-hydroxy cinnamic acid, 4-hydroxy-3-methoxy cinnamic acid, D-galacturonic acid, and polygalacturonic acid).

Some of the greater reductions in TOC could be traced to the formation of insoluble salts with the ferric ion, such as for the 3,4,5-trihydroxybenzoic acid (Figure 24d). This would not account, however, for the removal of *p*-hydroxybenzoic acid from solution since the ferric salt is soluble. Nor would the esters and alcohols, which do not form salts, be removed by this reaction.

The water solubility of the compounds, however, roughly correlates with their removal from solution with Fe^{3+} (Table 42). The compounds group into two classes, those with greater than 10 percent solubility in water and those with less than or equal to 1.5 percent solubility; the former group tends to have removals of 15 percent or less and those in the second class tend to have removals of 25 percent or greater (Figure 25).

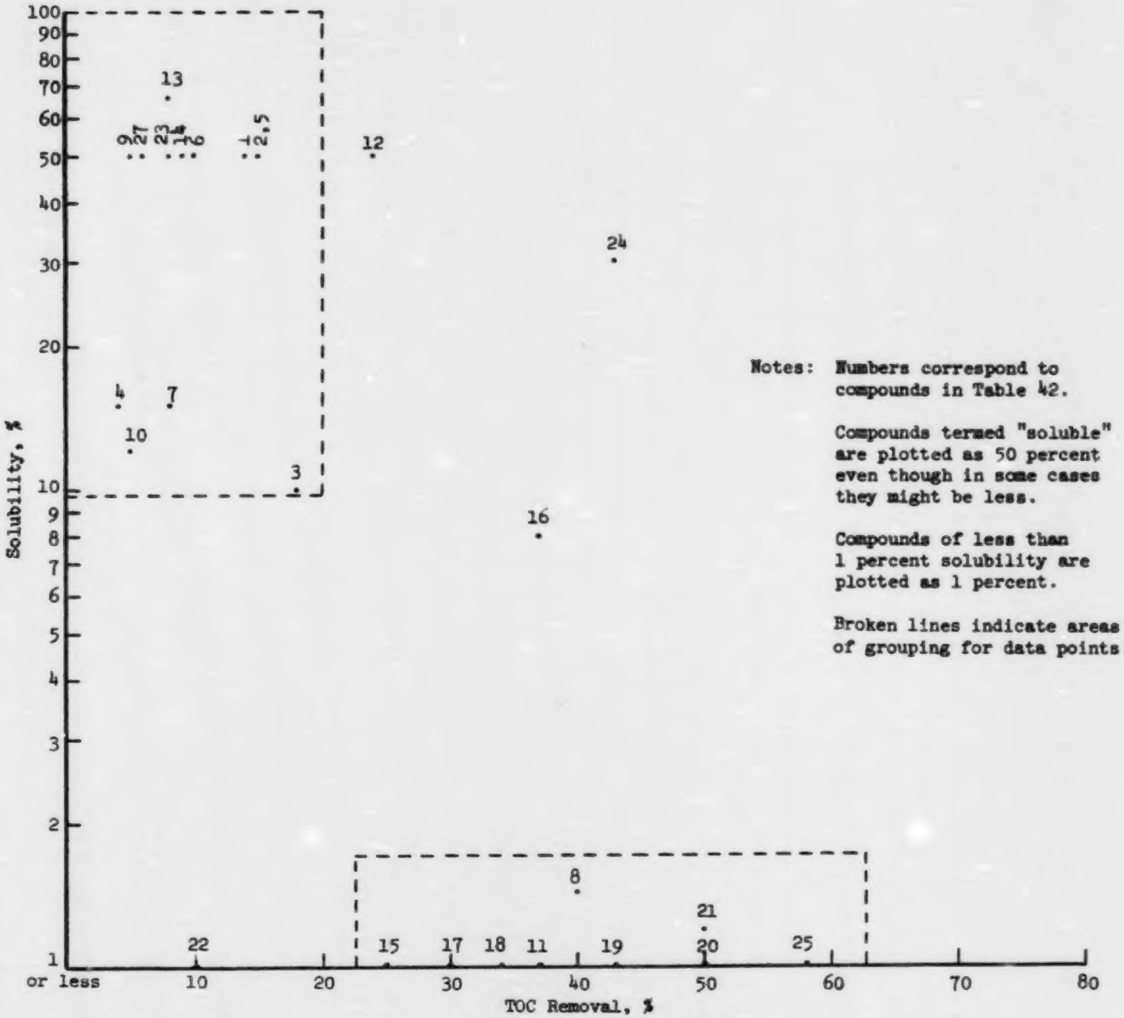
We must also consider not only reactions such as the cross-linking of starch phosphates with various cations and the increased complexing tendency observed for K^{+}, Ca^{++}, Zn^{++}, Cu^{++} and Fe^{+++} that Wettstein, Neukom and Deuel (19) studied extensively but also the oxalate or salicylate complexes with aluminum or iron as discussed by Stumm and Morgan (14). Stumm and Morgan studied the formation of ferric-hydroxo-complexes and found that they tended to polymerize with other charged molecules at rather exact pH's. Such interactions might be occurring in our jar tests.

Additional work would be required to pinpoint the effects on soluble BOD_5 removal by the organic compound chain lengths or branching, the presence of phenolic or carboxylic groups and the solubility of the individual compounds, all of which appear to have some important relationship to the overall soluble BOD_5 removal mechanism.

TABLE 42. SOLUBILITY IN WATER OF VARIOUS MODEL COMPOUNDS[a] AND THEIR REMOVAL IN JAR TESTS WITH Fe^{3+} AND PULP FIBERS[a]

Reference No.	Compound[a]	Solubility,[b] %	Removal,[a] %
1	Acetic acid	Miscible	14
2	Methyl acetate	Soluble	15
3	Ethyl acetate	10	18
4	Oxalic acid	15	4
5	Lactic acid	Miscible	15
6	Methyl lactate	Decomp. in H_2O	10
7	Raffinose	15	8
8	Adipic acid	1.44	40
9	2-Pentanol	Soluble	5
10	Tertiary amyl alcohol	12	5
11	Fumaric acid	0.63	37
12	Maleic acid	Freely soluble	24
13	Malonic acid	66	8
14	Tartronic acid	Very soluble	9
15	Benzylmalonic acid	Not given; probably less than 1%	25
16	Succinic acid	8	37
17	Benzoic acid	0.3	30
18	p-Hydroxybenzoic acid	0.8	34
19	o-Hydroxybenzoic acid	0.2	43
20	p-Methylbenzoic acid	Slightly soluble	50
21	3,4,5-Trihydroxybenzoic acid	1.2	50
22	Vanillin	1	10
23	Resorcinol	50	8
24	Catechol	30	43
25	p-Hydroxycinnamic acid	Not given; probably less than 1%	58
26	Ferulic acid	?	73
27	D-galacturonic acid	Soluble	6
28	Polygalacturonic acid	?	99

[a] Model compounds and % removal shown in Fig. 23-24e.
[b] Solubility in water, from Merck Index, 7th edition.



Notes: Numbers correspond to compounds in Table 42.

Compounds termed "soluble" are plotted as 50 percent even though in some cases they might be less.

Compounds of less than 1 percent solubility are plotted as 1 percent.

Broken lines indicate areas of grouping for data points.

Figure 25. The model compounds shown in Figures 23-24e cluster in two groups on the basis of solubility in water and removability with Fe^{3+}.

SECTION IX

AREAS FOR COST REDUCTIONS

This research study on the mechanisms for the BOD_5 removal in clarifiers was not intended to cover comparative process economics. However, evaluation of the data obtained in the laboratory and practical observations in the field studies indicate that improvements in the clarification process will reduce costs. Studies on the flows from individual process sewers demonstrated that treatment which removes soluble BOD_5 prior to the clarifier is likely also to reduce the overall cost for the total system of treatment.

SEPARATION OF FLOWS ADVERSELY AFFECTING CLARIFICATION EFFICIENCY

There are several ways to reduce costs, and careful control of the quality of the in-flow to the clarifier is one of them. Proper clarifier performance (reduction of suspended solids, COD, BOD_5, etc.) is dependent upon sedimentation and flocculation properties of the influent flow. The input of lignin and other pulping and bleaching constituents having colloidal and dispersant properties is of particular concern. The reduction or elimination of flows containing such materials, and particularly the containment and separate treatment of large spills of them, should substantially improve the clarification efficiency and should have high priority in programs for cost reduction in waste treatment. Revised handling should produce the following substantial economies:

1. The capital investment for a clarification system will be less when the clarifier size is reduced;
2. Reagent and other operating charges will be less as clarifier efficiency improves;
3. Clarifier performance in all categories, including the amount of BOD_5 removal, should be greatly improved;
4. Although no measurements were undertaken in this study, sludge dewatering, sludge volume and sludge disposal problems were apparent and should be subject for further development;
5. Needs and costs for subsequent (secondary biological) treatment may be significantly reduced in terms of capital cost and operating charges, and the need for secondary clarification may also be reduced.

OPTIMIZING THE TYPE AND AMOUNT OF CHEMICAL ADDITIVE

This project also showed the importance of optimizing the amounts and types of flocculating agents for various clarifier inflows. Different chemical additives are needed for different mills. Process fluctuations and changes affecting clarifier performance were apparent within the short term of each mill field trial.

Operating experience may make possible the development of routines for addition of chemicals when the effluents change. The rising trend toward development and use of computerized systems to control the manufacture of pulp and paper may logically extend to automated changes during effluent treatment.

Of the two mill clarifiers used in the field studies, one was utilizing chemical additives routinely and the other clarifier was well equipped to use flocculating chemicals. Capital costs for additional chemical feeding and mixing equipment would not be a major expense. Operating charges for the chemical additives that we used was about 3¢ to 10¢ per 1000 gallons of clarifier inflow (Table 43). Since these chemicals might logically replace less efficient additives already being used, cost could be considerably less in actual practice. The efficient use of chemicals would, moreover, be expected to give a return in reduced overall waste treatment costs. The actual cost of chemical additives to remove soluble BOD_5 cannot be adequately assessed short of detailed engineering cost studies to fit the situations in each mill.

TABLE 43. CHEMICAL COSTS FOR CLARIFICATION

Type of flocculant	Required, mg/l	Cost,[a] ¢/1000 gallons
Fe^{3+}[b]	25	2.72
	50	5.44
	100	10.88
Alum[c]	100	3.13
	200	6.26
	300	9.39

---

[a] Addition of 0.75 mg/l Hercofloc 812.3 would add 0.5¢.

[b] As ferric chloride ($FeCl_3 \cdot 6H_2O$) at $90/ton.

[c] Aluminum sulfate·16 H_2O at $75/ton.

SECTION X

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SECTION XI

GLOSSARY

Alum — Aluminum sulfate.

BOD — Biochemical oxygen demand is based on the oxygen requirement of living organisms while utilizing components of the waste stream for growth and/or reproduction.

BOD_5 — The biochemical oxygen demand in a 5-day test period at 20°C.

CM — Chemimechanical pulping; this is based on a short chemical cook followed by mechanical refining to separate the fibers in the softened chips.

COD — Chemical oxygen demand is the measurement of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by strong chemical oxidants (e.g., chromic acid).

Colloid — A phase dispersion to such a degree that the surface forces become an important factor in determining its properties. General particles of colloid dimension are 0.001 to 1 micron.

Gel chromatography — A column chromatographic technique which fractionates molecules on the basis of molecular weight.

Hemicellulose — That fraction of plant stems which is made up of carbohydrate polymers other than cellulose.

Molecular exclusion — The mechanism of fractionation of molecules during gel chromatography. Larger molecules are restricted from diffusing into the gel matrix, thus taking less time to travel through the gel than smaller molecules.

Permeate — That portion of a solution passing through a membrane during reverse osmosis or ultrafiltration.

Reverse osmosis (RO) — Osmosis in reverse flow through a semipermeable membrane when external pressure in excess of the osmotic pressure is applied.

Soluble — As used in this report is that portion of the solution (solvent and solute) passing through a 0.45 μm filter under 100 psig nitrogen pressure.

Zeta potential — That portion of the total potential drop between the surface of the solid and the suspending liquid that is contributed by the charge potential between the liquid adhering to the wall of the particle and the movable liquid.

SECTION XII

APPENDICES

APPENDIX A: COMPANIES AND AGENCIES SUPPORTING PHASE I STUDIES

Bergstrom Paper Company

Hammermill Paper Company

Hoerner Waldorf Corporation

Kimberly-Clark Corporation

The Mead Corporation

NCR-Appleton Papers Division

Nekoosa Edwards Paper Company, Inc.

Potlatch Corporation

The Proctor & Gamble Company

Scott Paper Company

Wausau Paper Mills Company

Department of Natural Resources, State of Wisconsin
U.S. Environmental Protection Agency

TABLE B-1. CLARIFIER STUDIES WITH HERCOFLOC 812.3 (0.75 mg/l) AT MOSINEE PAPER CORPORATION

			Influent (A)					Effluent (B)					% Reduction			
					BOD_5, mg/l					BOD_5, mg/l				BOD_5		
Date	Day	Composite^a	pH	Sus. Sol., mg/l	Total	Soluble	Color Units	pH	Sus. Sol., mg/l	Total	Soluble	Color Units	Sus. Sol.	Total	Soluble	Color
Due to Mechanical Difficulties - No "Sets of Samples" were taken from 1/15 - 2/5/75 (1st to 22nd day)																
2/6	23	1	7.70	167	96	72	45	7.59	45	85	88	52	73.0	11.4	-22.2	-13.5
		2	7.62	202	127	120	93	7.90	50	120	108	97	75.2	5.5	10.0	-4.1
		M	7.82	196	116	96	97	7.61	41	94	87	52	79.1	19.0	9.4	46.4
		Mill^b	—	218	90	—	—	—	56	51	—	—	74.3	43.3	—	—
2/7	24	1	7.90	273	111	110	93	7.91	74	121	106	74	72.9	-9.0	3.6	20.4
		2	7.81	211	137	131	103	7.82	45	113	92	74	78.7	17.5	29.8	28.2
		M	7.52	266	132	123	82	7.61	44	113	99	63	83.4	14.4	19.5	23.2
		Mill^b	—	260	84	—	—	—	56	63	—	—	78.5	25.0	—	—
2/11	28	1	7.60	358	372	179	374	9.73	101	365	246	5040	71.8	-1.9	-37.4	-124.7
		2	7.50	359	177	142	86	8.40	153	149	150	118	57.4	15.8	-5.6	-37.2
		M	9.20	257	262	254	1580	9.09	53	222	217	1420	79.4	15.3	14.6	10.1
		Mill^b	—	249	249	—	—	—	71	195	—	—	71.5	21.7	—	—
2/12	29	1	7.39	416	152	122	50	7.40	106	134	127	45	74.5	11.8	-4.1	10.0
		2	7.70	344	188	142	144	6.88	97	143	124	56	71.8	23.9	12.7	61.1
		M	8.40	502	174	166	38	7.59	88	141	144	81	82.5	19.0	13.2	-53.1
		Mill^b	—	338	141	—	—	—	66	114	—	—	80.5	19.1	—	—
2/13	30	1	8.53	364	138	120	56	8.29	114	124	126	63	68.7	10.1	-5.0	-12.5
		2	8.69	256	204	162	284	8.38	131	162	142	168	48.8	20.6	12.3	40.8
		M	8.21	290	152	129	104	7.89	85	130	120	115	70.5	14.5	7.0	10.6
		Mill^b	—	160	111	—	—	—	73	108	—	—	54.4	2.7	—	—
2/14	31	1	8.40	228	170	114	63	8.12	73	111	114	49	68.0	34.7	0	22.2
		2	8.21	266	150	127	48	8.19	49	120	125	38	81.6	20.0	0	15.6
		M	8.12	289	128	97	86	7.70	37	124	110	59	87.2	2.9	-13.4	31.4
		Mill^b	—	210	99	—	—	—	57	75	—	—	72.8	24.2	—	—

[a] Composites
A1 — from 7:30 a.m. to 7:30 p.m.
A2 — from 7:30 p.m. to 7:30 a.m.
B1 and B2 — Two hours after A's to allow for holding time
M — 24-hour mill composite (7:30 AM) analyzed in Appleton labs.

[b] Same as (M) analyzed at mill.

TABLE B-2. CLARIFIER STUDY WITH ALUM (200 mg/l) PLUS HERCOFLOC 812.3 (0.75 mg/l) AT MOSINEE PAPER CORPORATION

			Influent (A)					Effluent (B)					% Reduction			
					BOD_5, mg/l					BOD_5, mg/l				BOD_5		
Date	Day	Composite[a]	pH	Sus. Sol., mg/l	Total	Soluble	Color Units	pH	Sus. Sol., mg/l	Total	Soluble	Color Units	Sus. Sol.	Total	Soluble	Color
2/18	35	1	9.40	188	112	108	108	8.01	10	78	80	4	94.7	30.4	25.9	96.3
		2	8.78	54	130	106	74	5.80	8	77	85	0	85.2	40.8	19.8	100.0
		M	9.29	342	128	127	652	8.58	61	74	76	97	82.2	42.2	40.2	85.1
		Mill[b]	—	464	81	—	—	—	64	66	—	—	86.2	18.5	—	—
2/19	36	1	8.51	213	146	128	203	7.32	4	104	98	19	98.1	28.8	23.4	90.6
		2	9.11	222	190	174	888	8.65	0.5	108	107	41	99.9	43.2	38.5	95.5
		M	8.80	218	150	112	356	7.72	63	136	108	188	71.1	9.3	3.6	47.2
		Mill[b]	—	234	99	—	—	—	74	69	—	—	68.4	30.3	—	—
2/20	37	1	7.30	119	103	73	80	8.55	15	92	94	22	87.4	10.7	-28.8	72.5
		2	8.11	136	139	117	310	6.80	18	90	88	15	86.8	35.2	24.8	95.2
		M	8.41	153	116	99	170	7.78	40	102	78	125	73.8	12.1	21.2	26.5
		Mill[b]	—	216	159	—	—	—	62	135	—	—	71.3	15.1	—	—
2/21	38	1	7.83	278	116	112	71	8.19	44	104	99	52	84.2	10.3	11.6	26.8
		2	8.08	289	140	127	133	7.62	70	126	106	74	75.8	10.0	16.5	44.4
		M	7.59	206	112	88	56	7.39	55	104	87	74	73.3	7.1	-1.1	-32.1
		Mill[b]	—	204	129	—	—	—	58	108	—	—	71.6	16.3	—	—
2/26	43	1	7.41	221	114	112	41	8.84	60	100	94	4	72.8	12.3	16.1	90.2
		2	7.58	176	113	94	23	8.71	7	113	98	0	96.0	0	4.2	100.0
		M	7.54	215	140	96	31	7.40	60	104	84	15	72.1	25.7	8.3	51.6
		Mill[b]	—	283	114	—	—	—	79	105	—	—	82.2	7.9	—	—
2/27	44	1	7.55	155	108	108	120	6.90	24	96	92	22	84.5	11.1	14.8	81.7
		2	7.78	153	100	104	122	6.68	18	87	85	12	88.2	13.0	18.3	90.2
		M	7.65	180	110	104	124	7.25	62	86	93	78	65.6	21.8	10.6	37.8
		Mill[b]	—	248	96	—	—	—	57	75	—	—	77.0	21.9	—	—
2/28	45	1	7.53	82	96	95	62	6.55	9	84	83	22	89.0	12.5	12.6	64.5
		2	7.70	130	94	92	80	6.20	15	83	80	12	88.5	11.7	13.0	85.0
		M	7.32	201	86	89	68	7.25	71	78	71	49	64.7	9.3	20.2	27.9
		Mill[b]	—	121	108	—	—	—	30	36	—	—	75.2	66.7	—	—

[a] Composites
A1 — from 7:30 a.m. to 7:30 p.m.
A2 — from 7:30 p.m. to 7:30 a.m.
B1 and B2 — Two hours after A's to allow for system holding time
M — 24-hour mill composite (7:30 AM) analyzed in Appleton labs.

[b] Mill — same as (M) analyzed by mill.

TABLE B-3. CLARIFIER STUDY WITH FERRIC CHLORIDE (100 mg/1 Fe^{3+}) PLUS HERCOFLOC 812.3 (0.75 mg/1) AT MOSINEE PAPER CORPORATION

			Influent (A)					Effluent (B)					% Reduction			
				Sus. Sol.,	BOD_5, mg/1		Color		Sus. Sol.,	BOD_5, mg/1		Color		BOD_5		
Date	Day	Composite[a]	pH	mg/1	Total	Soluble	Units	pH	mg/1	Total	Soluble	Units	Sus. Sol.	Total	Soluble	Color
3/4	49	1	7.85	189	190	93	78	4.10	18	70	72	45	90.5	63.2	22.5	42.3
		2	8.75	136	244	138	130	3.93	30	124	106	30	77.9	49.2	23.2	76.9
		M	8.00	204	226	102	162	7.95	74	110	84	140	63.7	51.3	17.6	13.6
		Mill[b]	--	230	135	--	--	--	66	72	--	--	71.3	46.7	--	--
3/5	50	1	7.73	126	128	88	133	3.74	28	86	78	34	77.8	32.8	11.4	74.4
		2	8.51	199	158	117	204	2.69	83	83	78	27	58.3	47.5	33.3	86.8
		M	7.62	207	148	108	204	7.71	37	122	92	156	82.1	17.6	14.8	23.5
		Mill[b]	--	190	135	--	--	--	42	105	--	--	77.9	22.2	--	--
3/6	51	1	8.40	240	140	95	168	3.47	22	86	75	27	90.8	38.6	21.0	83.9
		2	7.61	169	142	88	74	3.18	6	88	76	12	96.4	38.0	13.6	83.8
		M	7.80	276	122	91	98	7.28	63	106	82	74	76.9	13.1	9.9	24.5
		Mill[b]	--	264	107	--	--	--	49	77	--	--	81.4	28.0	--	--
3/7	52	1	7.11	198	88	86	82	3.89	4	80	78	27	98.0	9.1	9.3	67.1
		2	7.31	213	94	76	56	3.89	2	92	79	19	99.1	2.1	-3.9	66.1
		M	7.22	204	91	74	100	7.18	75	96	70	60	63.2	-7.0	5.7	40.0
		Mill[b]	--	224	105	--	--	--	65	81	--	--	71.0	22.8	--	--
3/11	56	1	8.89	182	102	82	170	3.89	8	73	66	15	95.6	28.4	19.5	91.2
		2	7.81	209	114	98	60	4.18	5	78	77	19	97.6	31.6	21.4	68.3
		M	7.70	197	102	81	111	7.41	65	109	87	118	67.0	-6.8	-7.4	-6.0
		Mill[b]	--	264	111	--	--	--	51	93	--	--	80.7	16.2	--	--
3/12	57	1	7.69	228	170	144	126	3.50	9	120	79	30	96.0	29.4	45.1	76.2
		2	7.19	22	109	102	38	4.39	4	70	71	27	81.8	35.8	30.4	28.9
		M	7.70	258	130	100	71	7.31	45	94	94	38	82.6	27.7	6.0	46.5
		Mill[b]	--	236	132	--	--	--	39	81	--	--	83.5	38.6	--	--
3/13	58	1	8.26	220	160	136	192	4.71	12	90	90	52	94.5	43.8	33.8	72.9
		2	7.99	199	161	127	174	4.11	13	100	99	52	94.0	37.9	22.0	70.1
		M	7.82	206	140	114	222	7.51	81	121	112	122	60.7	13.6	1.8	45.0
		Mill[b]	--	294	141	--	--	--	57	126	--	--	80.1	10.6	--	--
3/14	59	1	7.10	192	122	101	115	4.18	15	92	83	38	92.2	24.6	17.8	67.0
		2	7.29	128	128	102	159	3.51	4	86	81	34	96.9	32.8	20.6	78.6
		M	7.41	245	142	110	126	7.19	59	129	110	108	75.9	9.2	0	14.3
		Mill[b]	--	176	144	--	--	--	59	108	--	--	66.5	25.0	--	--

[a] Composites — all on 60-minute cycle
A1 — from 7:30 a.m. to 7:30 p.m.
A2 — from 7:30 p.m. to 7:30 a.m.
B1 and B2 — Two hours after A's to allow for system holding time
M — 24-hour mill composite analyzed at Appleton labs.

[b] Mill — same as (M) analyzed by mill.

TABLE E-4. CLARIFIER STUDY WITH FERRIC SULFATE AND HERCOFLOC AT MOSINEE PAPER CORPORATION

			Influent (A)					Effluent (B)					% Reduction			
				Sus. Sol.,	BOD$_5$, mg/l		Color		Sus. Sol.,	BOD$_5$, mg/l		Color		BOD$_5$		
Date	Day	Composite[a]	pH	mg/l	Total	Soluble	Units	pH	mg/l	Total	Soluble	Units	Sus. Sol.	Total	Soluble	Color
D. Ferric Sulfate (50-100 mg/l Fe^{+3})																
3/18	63	1	8.01	187	192	138	332	6.16	126	124	101	38	32.6	35.4	26.8	88.6
		2	7.28	214	147	110	82	6.32	105	120	98	38	51.4	18.4	10.9	53.6
		M	7.41	359	221	131	126	7.30	57	144	132	211	84.1	34.8	-0.8	-67.5
		Mill[b]	--	246	195	--	--	--	51	93	--	--	75.2	52.3	--	--
3/19	64	1	7.62	286	158	130	118	5.30	22	100	95	38	92.3	36.7	26.9	67.8
		2	7.22	202	136	116	111	4.56	18	93	88	45	91.1	31.6	24.1	59.4
		M	7.40	178	146	113	108	7.01	73	121	106	163	59.0	17.1	6.2	-50.9
		Mill[b]	--	226	122	--	--	--	60	110	--	--	73.4	9.8	--	--
3/20	65	1	8.09	191	180	148	273	4.67	55	122	107	45	71.2	32.2	27.7	83.5
		2	7.22	168	173	124	145	3.61	10	86	83	52	94.0	50.3	33.1	64.1
		M	7.07	149	186	144	163	7.11	74	140	122	160	50.3	24.7	15.3	1.8
		Mill[b]	--	175	140	--	--	--	59	86	--	--	66.3	38.6	--	--
3/21	66	1	7.40	200	165	135	122	3.96	8	106	98	55	96.0	35.8	27.4	54.9
		2	7.20	178	139	104	68	3.32	7	89	86	70	96.1	36.0	17.3	-2.9
		M	7.33	224	170	116	90	7.19	62	126	106	90	72.3	25.9	8.6	0
		Mill[b]	--	218	120	--	--	--	54	60(?)	--	--	75.2	50.0(?)	--	--
E. Base Line (Hercofloc 812.3 at 0.75 mg/l)																
3/25	70	1	11.01	341	119	91	52	11.02	68	102	90	45	80.0	14.3	1.1	13.5
		2	7.91	190	134	104	31	7.81	23	112	112	31	88.0	16.4	-7.7	0
		M	8.95	241	132	100	56	8.26	61	88	86	52	74.7	33.3	14.0	7.1
		Mill[b]	--	278	93	--	--	--	63	63	--	--	77.3	32.2	--	--
3/26	71	1	7.99	239	170	146	41	7.80	36	170	114	41	84.9	0	21.9	0
		2	8.06	182	138	127	34	7.78	24	112	112	34	86.8	18.8	11.8	0
		M	7.81	262	--	114	38	7.51	46	125	112	38	84.0		1.8	0
		Mill[b]	--	300	92	--	--	--	50	47	--	--	83.3	48.9	--	--
3/27	72	1	8.32	137	172	130	103	8.41	51	182	128	100	62.8	-5.8	1.5	2.9
		2	8.13	235	146	130	192	8.14	39	125	124	296	83.4	14.4	4.6	-54.2
		M	8.19	245	192	122	150	7.84	57	132	104	103	76.7	31.2	14.8	31.3
		Mill[b]	--	192	108	--	--	--	51	57	--	--	73.4	47.2	--	--
3/28	73	1	6.28	177	184	127	332	8.01	31	166	139	460	82.5	9.8	-9.4	-38.6
		2	8.51	189	150	134	328	7.99	48	125	124	251	74.6	16.7	7.5	23.5
		M	9.21	253	158	120	318	8.32	62	120	110	278	75.5	24.0	8.3	12.6
		Mill[b]	--	260	117	--	--	--	43	120	--	--	83.5	-2.6	--	--

[a] Composites — A1, A2, B1, and B2 on 30-minute cycle
A1 — from 7:30 a.m. to 7:30 p.m.
A2 — from 7:30 p.m. to 7:30 a.m.
B1 and B2 — 90 minutes allowed for system holding time
M — 24-hour mill composite analyzed at Appleton labs.

[b] Mill — same as (M) analyzed by mill.

TABLE B-5. CLARIFIER STUDY WITH SULFURIC ACID, SULFURIC ACID PLUS POLYMER, AND FERROUS SULFATE PLUS POLYMER AT MOSINEE PAPER CORPORATION

			Influent (A)					Effluent (B)					% Reduction			
				Suc. Sol., mg/1	BOD$_5$, mg/1		Color Units		Sus. Sol., mg/1	BOD$_5$, mg/1		Color Units		BOD$_5$		
Date	Day	Composite[a]	pH		Total	Soluble		pH		Total	Soluble		Sus. Sol.	Total	Soluble	Color
F. Sulfuric Acid (pH adjustment only)																
4/1	77	1	8.61	270	320	176	640	6.51	193	248	150	92	28.5	22.5	14.8	85.6
		2	8.53	332	201	151	432	6.19	113	143	112	52	66.0	28.8	25.8	88.0
		M	9.72	307	211	177	960	9.51	50	140	125	318	83.7	33.6	29.4	66.9
		Mill[b]	--	302	--	--	--	--	62	--	--	--	79.5	--	--	--
4/2	78	1	7.61	331	148	124	67	6.18	131	114	98	41	60.4	23.0	21.0	38.8
G. Sulfuric Acid + Polymer																
	78	2	7.91	294	120	102	74	5.65	57	88	76	23	80.6	26.7	25.5	68.9
		M	7.79	260	114	102	59	7.40	68	109	92	81	73.8	4.4	9.8	-37.3
		Mill[b]	--	266	--	--	--	--	36	--	--	--	86.5	--	--	--
H. Ferrous Sulfate (100 mg Fe^{+2}/1) + Polymer																
4/3	79	1	7.70	271	150	126	160	5.19	183	106	92	322	32.5	29.3	27.0	-101.2
		2	8.72	177	144	114	296	7.61	169	148	106	45	4.5	-2.8	7.0	84.8
		M	8.19	227	140	120	200	7.30	83	104	96	168	63.4	25.7	20.0	16.0
		Mill[b]	--	224	--	--	--	--	52	--	--	--	76.8	--	--	--
4/4	80	1	8.61	222	172	137	3600	5.34	117	144	94	136	47.3	16.3	31.4	96.2
		2	7.62	184	138	112	200	5.59	164	90	78	207	10.9	34.8	30.4	-3.5
		M	7.40	275	216	136	118	7.19	57	143	108	185	79.3	33.8	19.1	-56.8
		Mill[b]	--	356	--	--	--	--	45	--	--	--	87.4	--	--	--

[a] Composites — A1, A2, B1, and B2 on 30-minute cycle
A1 — from 7:30 a.m. to 7:30 p.m.
A2 — from 7:30 p.m. to 7:30 a.m.
B1 and B2 — 90 minutes allowed for system holding time
M — 24-hour mill composite analyzed at Appleton labs.

[b] Mill — Same as (M) analyzed by mill.

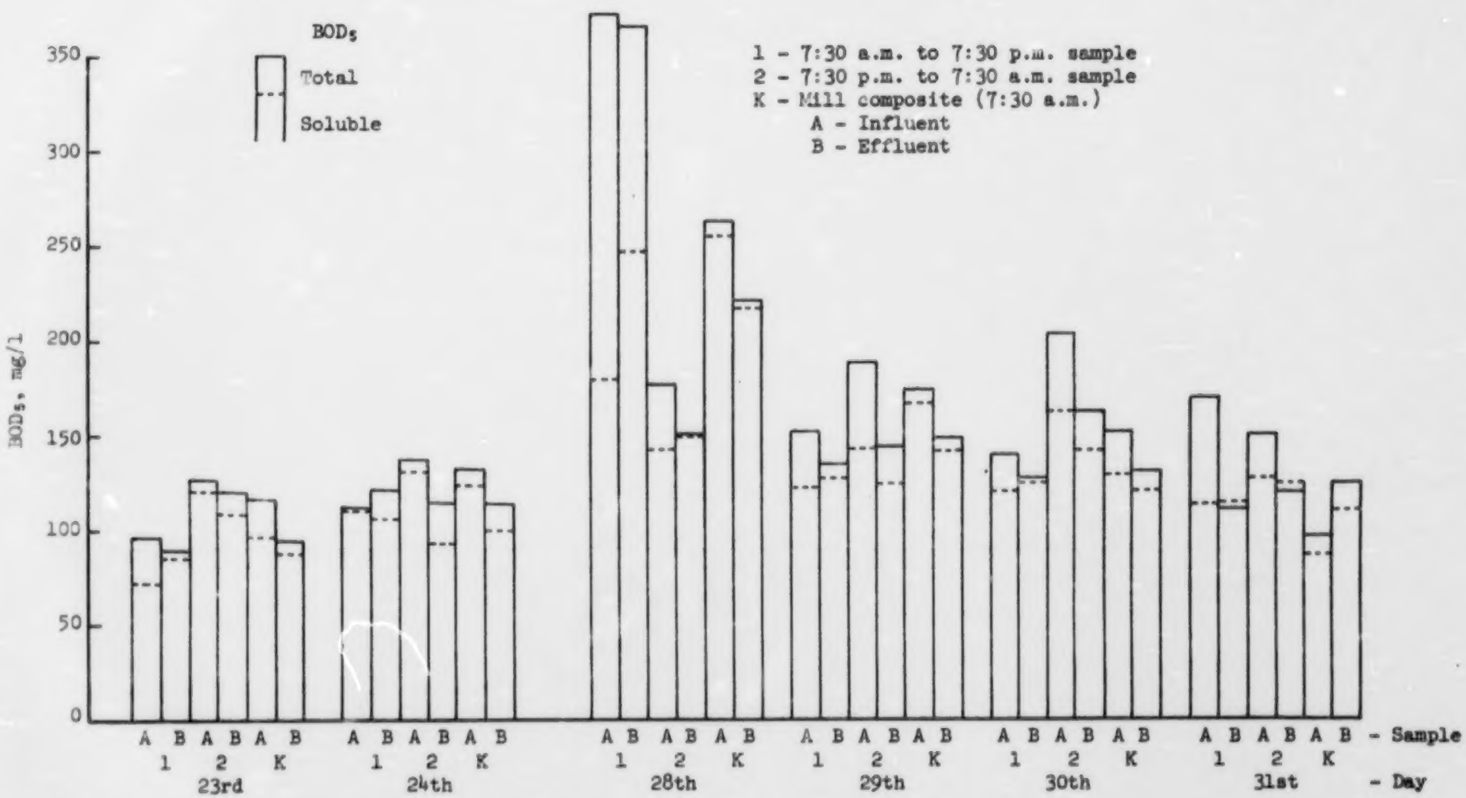

A. Base Line (0.75 mg/1 Hercofloc 812.3) - Mosinee

Figure B-1. BOD₅ reduction during clarification with Hercofloc

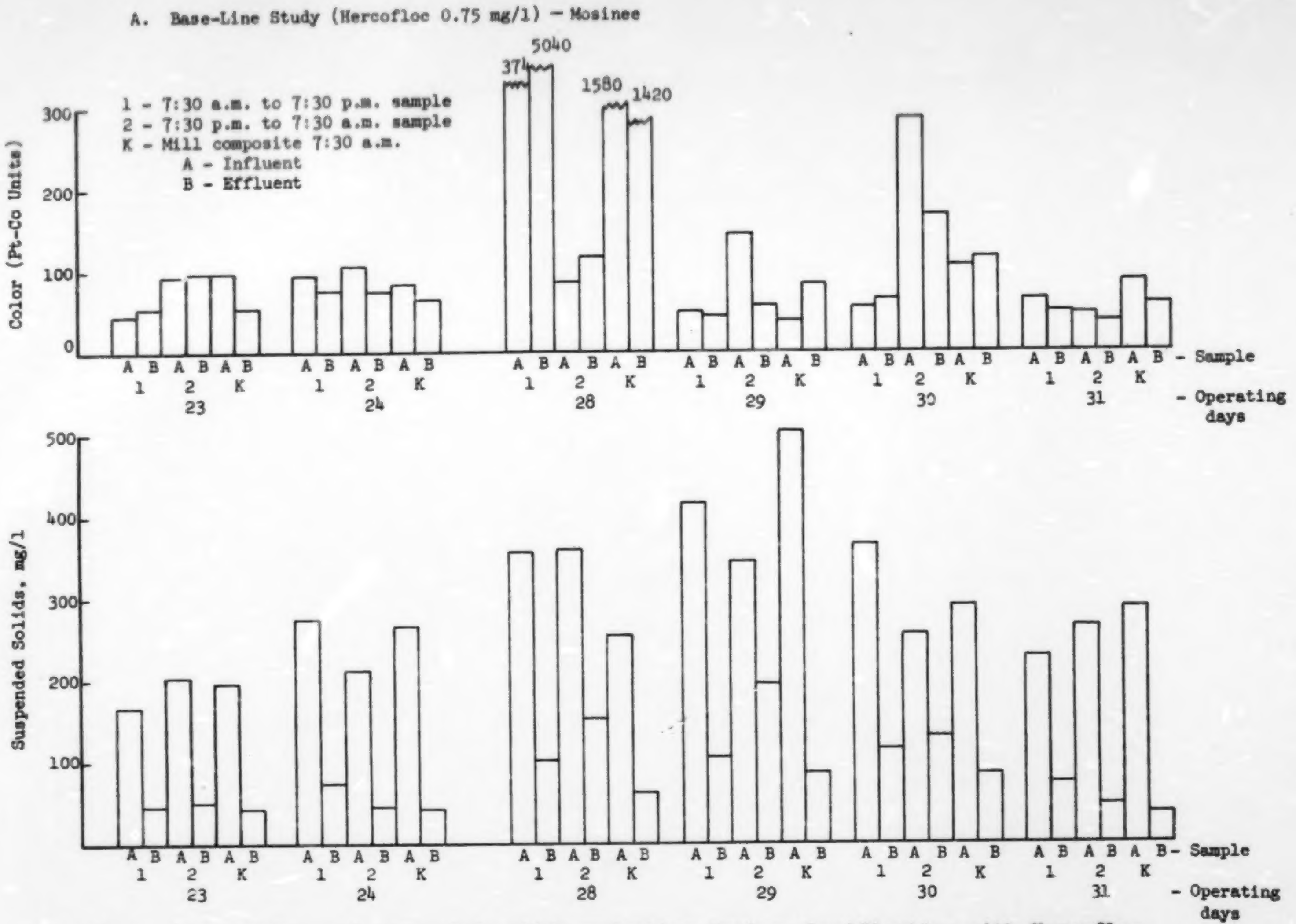

A. Base-Line Study (Hercofloc 0.75 mg/1) — Mosinee

Figure B-2. Color and suspended solids reduction during clarification with Hercofloc.

B. Alum Addition (200 mg/1) — Mosinee

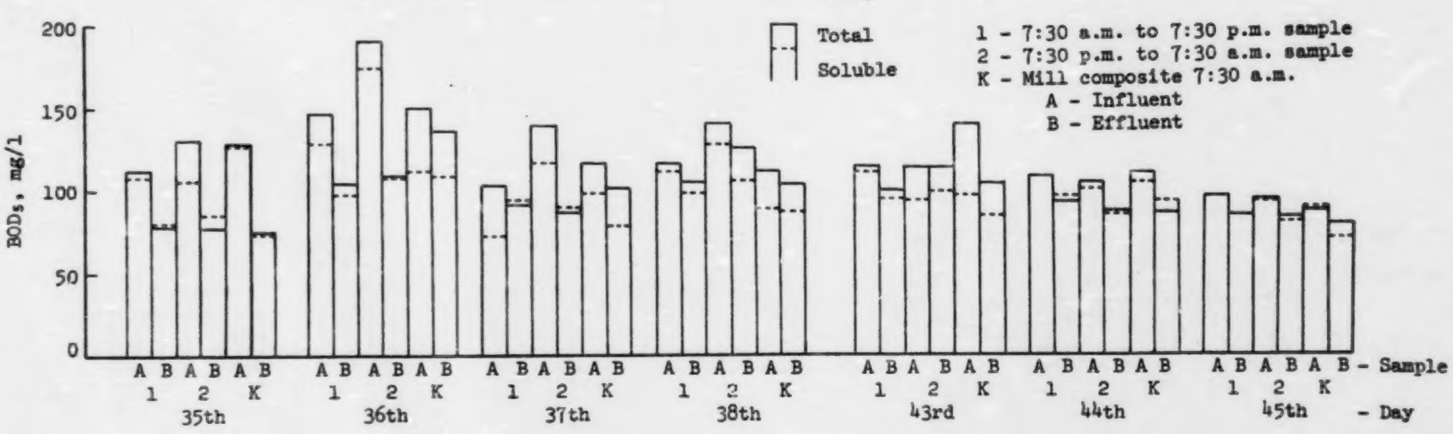


Figure B-3. BOD₅ reduction during clarification with alum.

B. Alum Addition (200 mg/1) — Mosinee

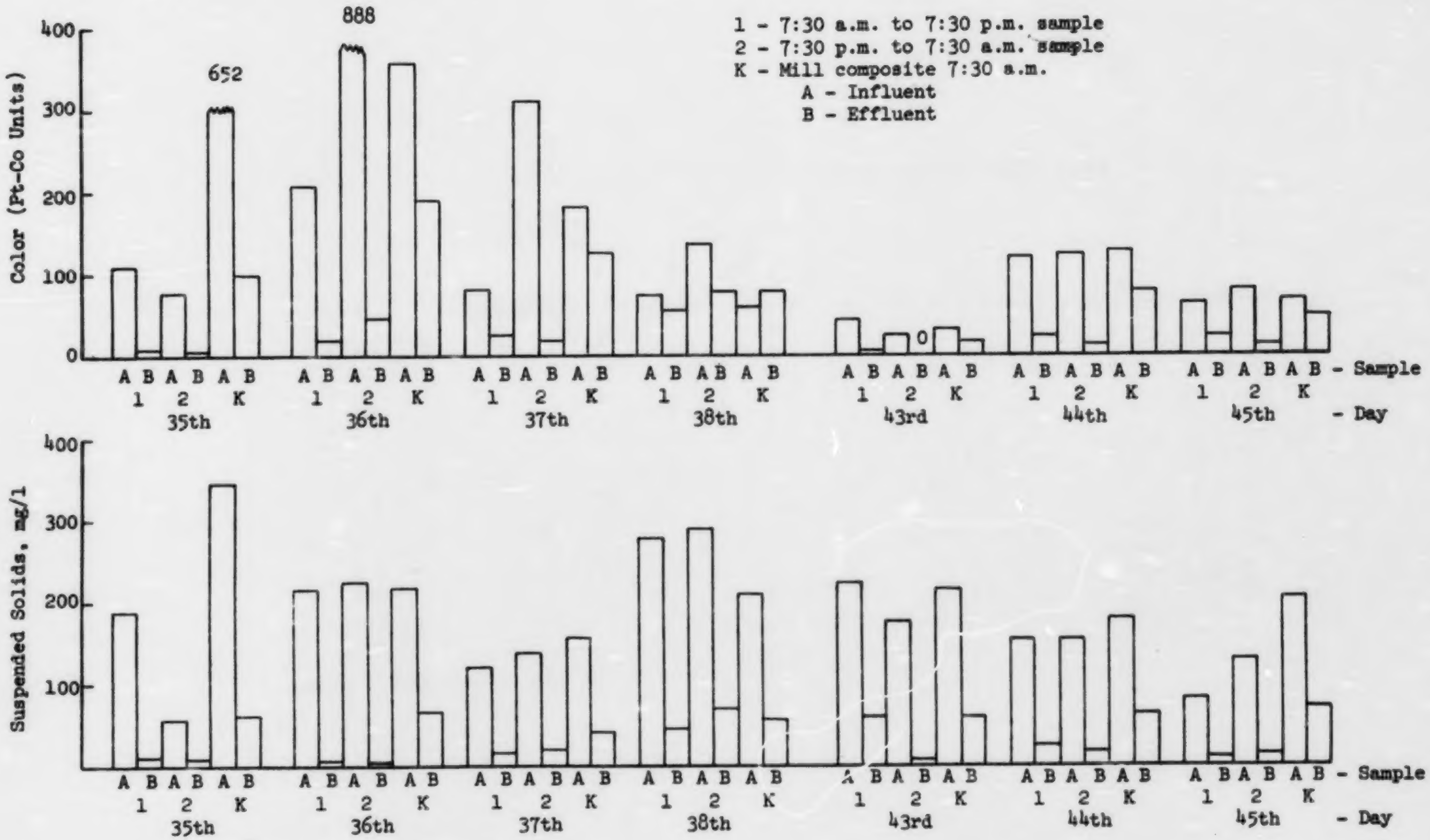


Figure B-4. Color and suspended solids reduction during clarification with alum.

C. Ferric Chloride Addition (100 mg/1 Fe^{+3}) — Mosinee

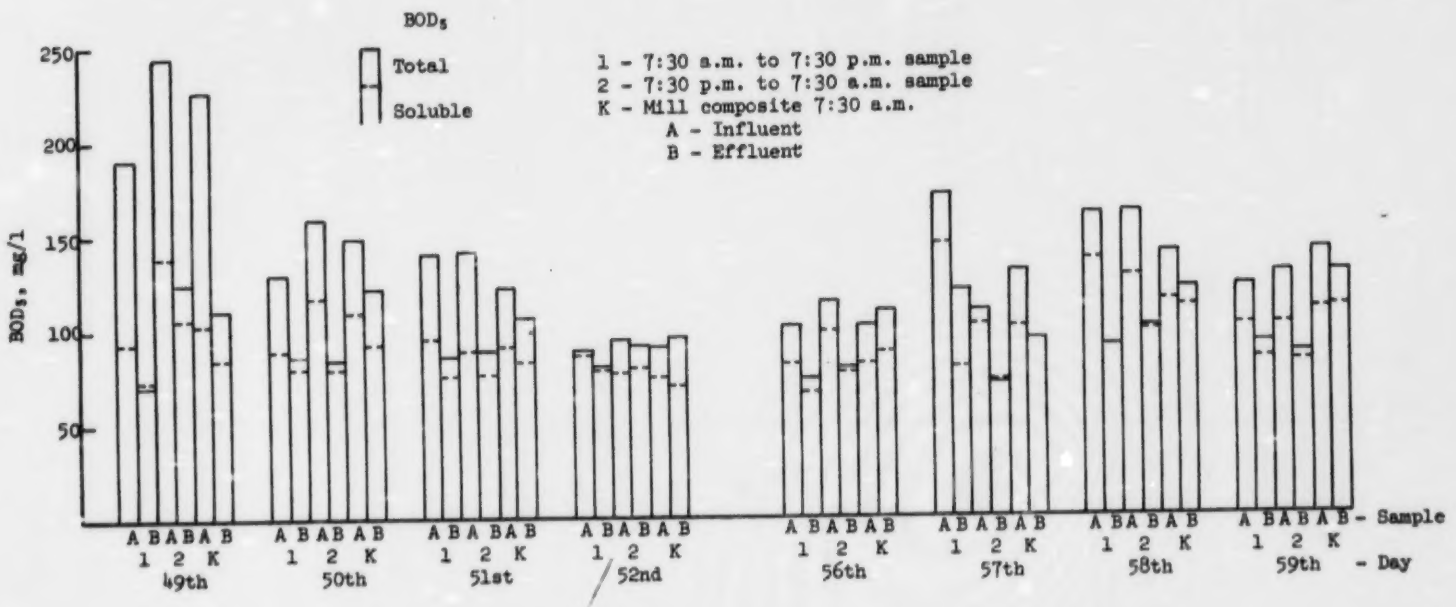


Figure B-5. BOD_5 reduction during clarification with ferric chloride.

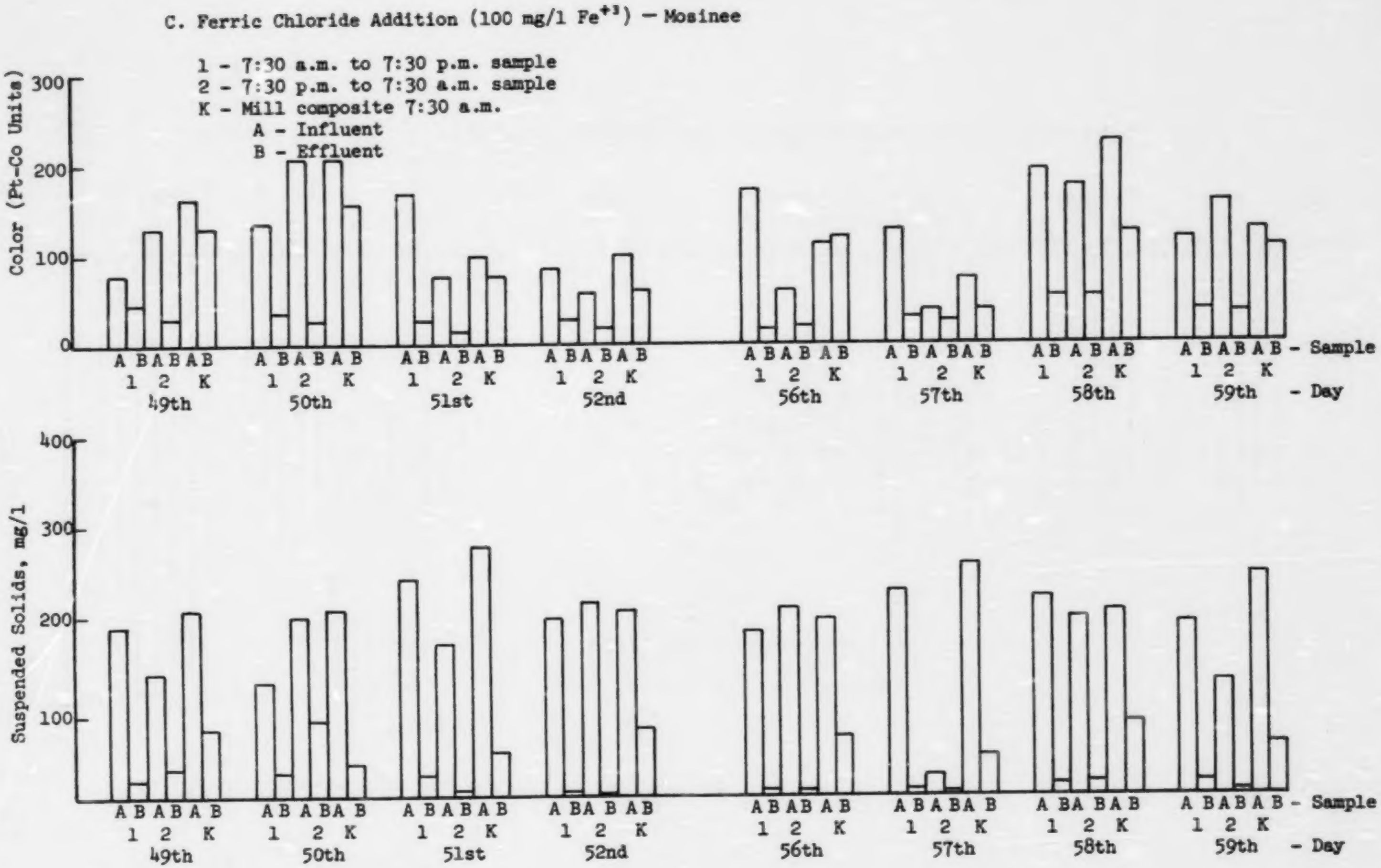
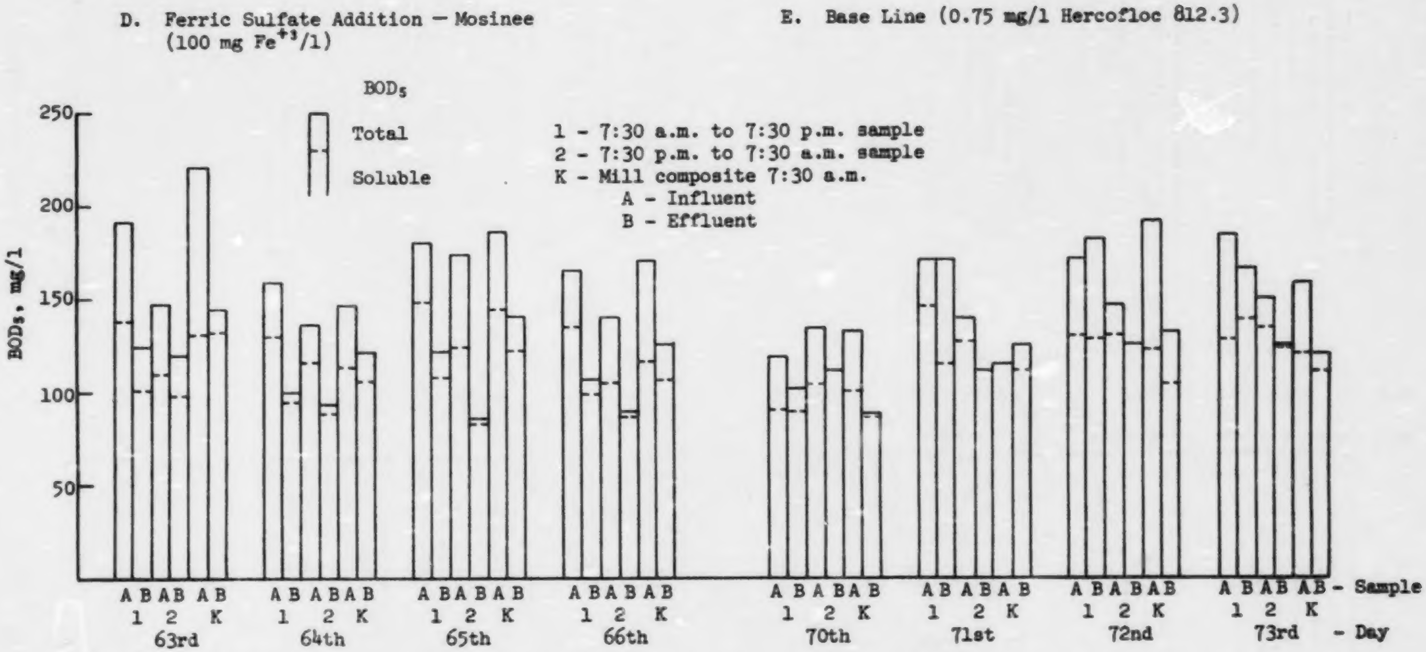


Figure B-6. Color and suspended solids reduction during clarification with ferric chloride.


D. Ferric Sulfate Addition — Mosinee (100 mg Fe^{+3}/1)

E. Base Line (0.75 mg/1 Hercofloc 812.3)

Figure B-7. BOD_5 reduction during clarification with ferric sulfate.

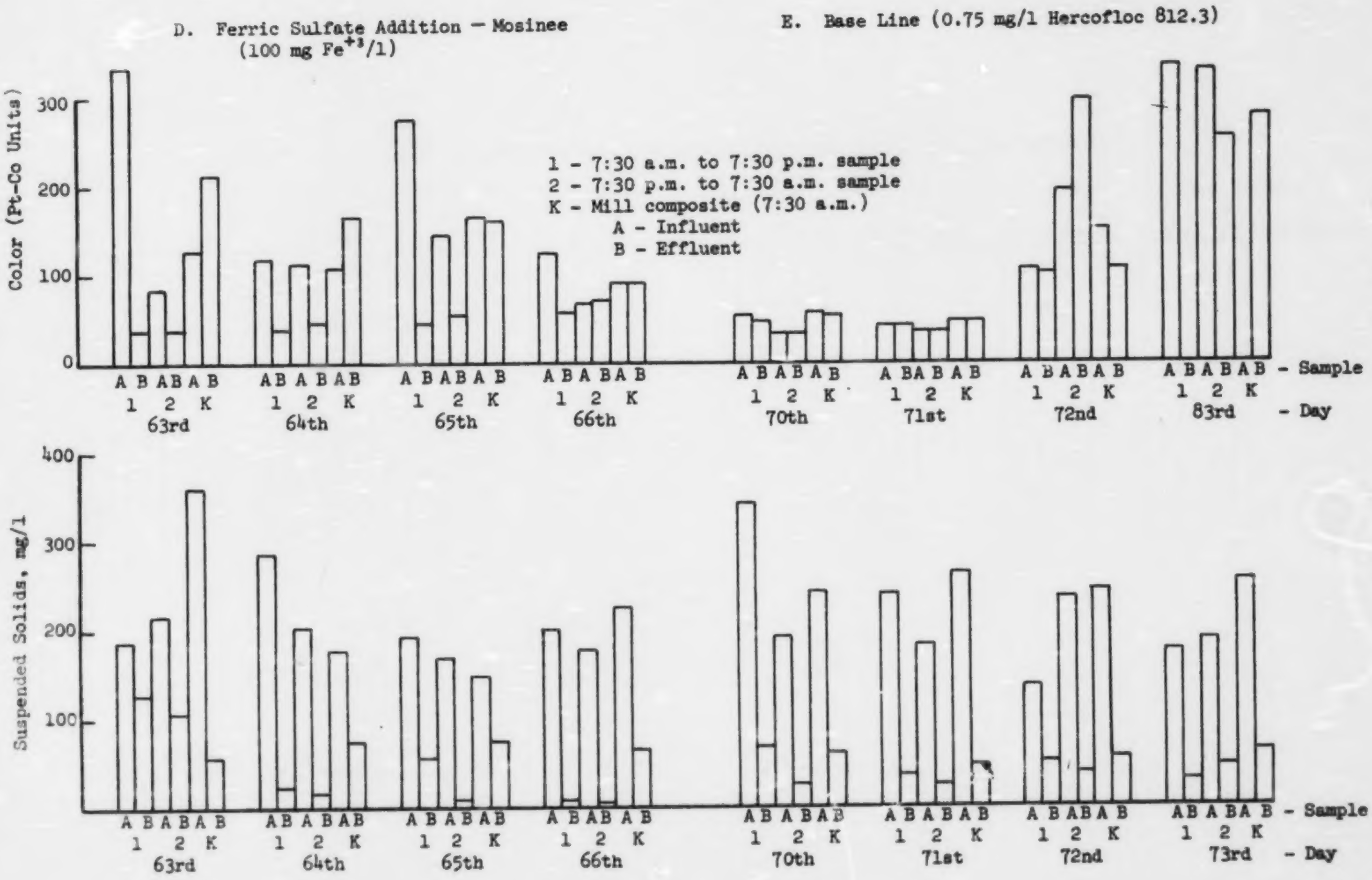


Figure B-8. Color and suspended solids reduction during clarification with ferric sulfate.

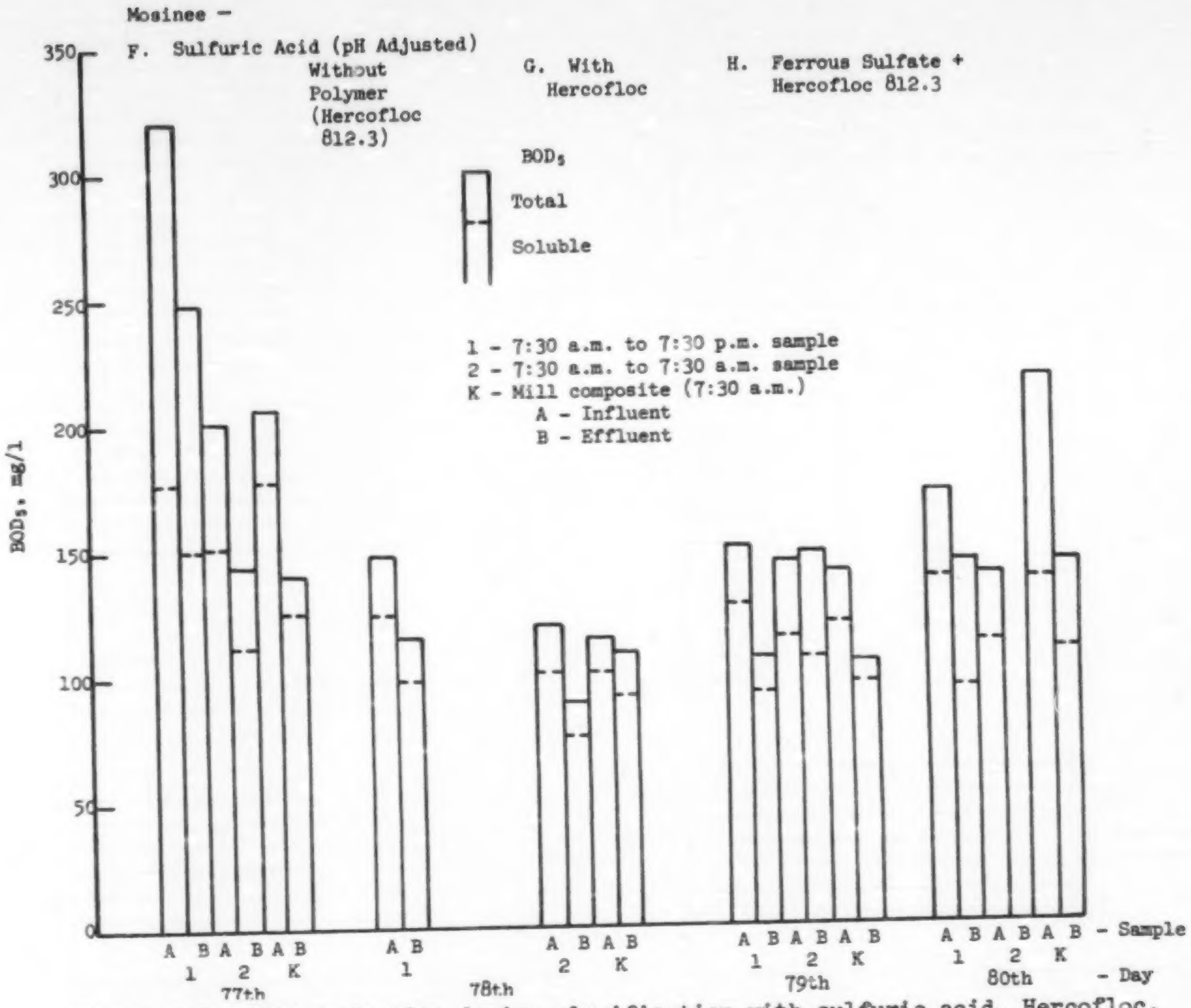


Figure B-9. BOD$_5$ reduction during clarification with sulfuric acid, Hercofloc, or ferrous sulfate plus Hercofloc.

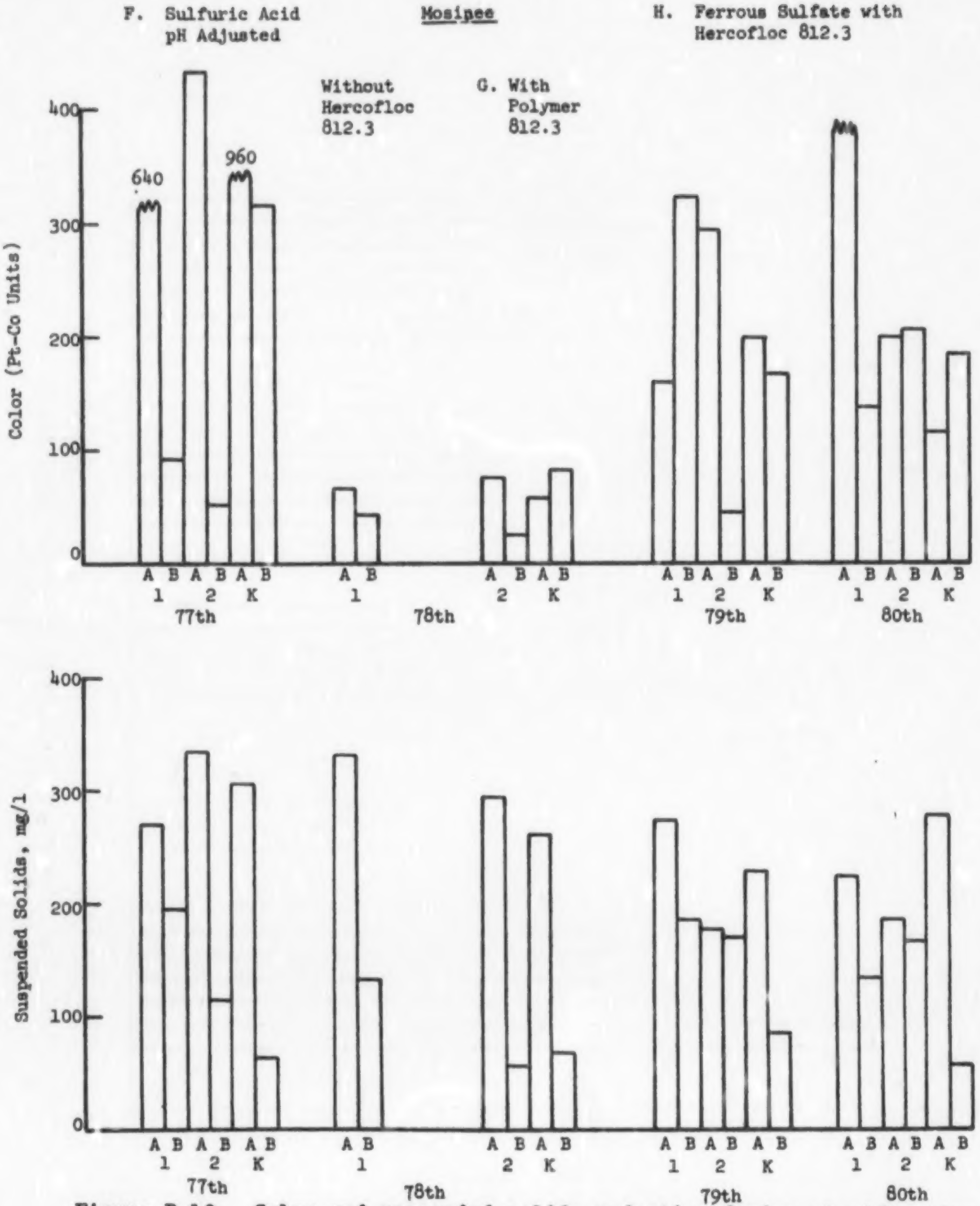


Figure B-10. Color and suspended solids reduction during clarification with sulfuric acid, Hercofloc, or ferrous sulfate plus Hercofloc.

TABLE C-1. CLARIFIER STUDY AT COMBINED LOCKS – BASE LINE (GRAVITY CLARIFICATION AFTER 0.010-INCH SIEVE) WITHOUT ADDITIVES[a],[b]

		Influent (C)						Effluent (D)						% Reduction			
			Sus. Sol. mg/l	BOD_5, mg/l		Color Units	Sol. Sol. mg/l		Sus. Sol. mg/l	BOD_5, mg/l		Color Units	Sol. Sol. mg/l		BOD_5		
Day	Composite	pH		Total	Soluble			pH		Total	Soluble			Sus. Sol.	Total	Soluble	Color
5	2	8.30	805	294	196	162		7.71	97	256	201	192		88.0	12.9	-2.6	-18.5
10	1	7.65	578	243	124	98		7.82	19	162	140	105		96.7	33.3	-12.9	-7.1
	2	7.45	749	312	190	122	668	7.55	44	208	176	150	680	94.1	33.3	7.4	-22.9
	M	-	664	278	157	110		7.91	56	234	159	145	596	91.9	15.8	0	-31.8
11	1	7.58	758	267	202	125		7.62	66	240	211	217		91.3	10.1	-4.4	-73.6
	2	7.71	814	322	233	215	796	7.71	37	282	238	202	850	95.4	12.4	-2.4	-40.5
	M	-	786	294	218	170		7.69	48	236	209	255	740	93.9	19.7	4.1	-50.0
12	1	7.35	621 (366)	176	127	100		7.50	19 (16)	140	128	75		96.9 (95.6)	20.4	0	25.0
	2	7.52	547 (330)	204	142	112		7.67	18 (14)	162	154	83		96.7 (95.8)	20.6	-8.4	26.0
	M	-	584 (348)	190	134	106		7.38	29 (22)	147	135	111		95.0 (93.7)	22.6	0	-4.5
13	1	7.65	638 (427)	352	268	175	838	7.65	44 (34)	270	254	200	850	93.1 (92.0)	23.3	5.2	-14.3
	2	7.60	643 (427)	355	252	185		7.71	31 (27)	286	271	205		95.2 (93.7)	19.4	-7.5	-9.8
	M	-	640 (427)	354	260	180		No Sample									
14	1	7.55	584 (397)	373	254	183		7.58	38 (25)	243	250	255		93.5 (93.7)	34.8	1.6	-39.3
17	1	7.40	541 (403)	300	216	195		7.40	72 (44)	222	220	230		86.7 (89.1)	26.0	-1.8	-17.9
	2	7.45	599 (450)	363	232	187	796	7.50	49 (31)	242	214	295	747	91.8 (95.3)	33.3	7.8	-57.8
	M	-	570 (426)	332	224	191		7.32	55 (32)	209	198	255	754	90.4 (92.5)	37.0	11.6	—
18	1	7.60	506 (373)	236	148	126		7.68	31 (23)	164	147	155		93.9 (93.8)	30.5	0.6	-23.0
	2	7.65	622 (484)	377	286	218		7.70	55 (41)	277	241	244		91.2 (91.5)	26.5	15.7	-11.9
	M	-	564 (428)	306	217	172		7.55	51 (36)	201	190	292		91.0 (91.6)	34.3	12.4	-69.8
19	1	7.59	415 (292)	217	138	204		7.58	36 (30)	181	162	196		91.3 (89.7)	16.6	-17.4	3.9
	2	7.62	435 (339)	380	319	322	996	7.59	76 (68)	374	338	377	1040	82.5 (79.9)	1.6	-5.6	-17.1
	M	-	425 (316)	298	228	263		7.60	51 (42)	268	238	302	798	88.0 (86.7)	10.1	-4.2	-14.8

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[a] Values in parentheses are volatile suspended solids.
[b] Underscored values are based on average of IPC influent samples.

TABLE C-2. CLARIFIER STUDY AT COMBINED LOCKS – FERRIC CHLORIDE (75 mg/1 Fe^{3+}) WITHOUT POLYMER[a,b]

		Influent (C)						Effluent (D)						% Reduction			
				BOD$_5$, mg/1						BOD$_5$, mg/1					BOD$_5$		
Day	Composite[c]	pH	Sus. Sol., mg/1	Total	Soluble	Color Units	Sol. Sol., mg/1	pH	Sus. Sol., mg/1	Total	Soluble	Color Units	Sol. Sol., mg/1	Sus. Sol.	Total	Soluble	Color
22	1	7.35	455 (337)	301	195	208		5.08	28 (24)	188	167	244		93.8 (93.2)[d]	37.5	14.4	-17.3
	2	7.38	562 (422)	332	246	252		6.10	181 (133)[d]	224	178	126		67.8 (68.5)	32.5	27.6	50.0
	M	—	—	316	220	230		7.22	61 (46)	232	212	266		—	26.6	3.6	-13.6
23	1	7.48	646 (472)	325	224	244	705	3.92	32 (18)	168	170	178	779	95.0 (96.2)	48.3	24.1	27.0
	2	7.40	291 (210)	306	230	288		4.89	14 (10)	197	190	122		95.2 (95.2)	35.6	17.4	22.9
	M	—	—	316	227	266		7.41	213 (171)	304	233	296	684	—	3.8	-2.6	-11.3
29	1	8.42	570 (415)	342	214	155	699	5.21	22 (17)	172	155	133	685	96.1 (95.9)	49.7	27.6	14.2
	2	7.79	606 (428)	311	195	152		4.69	20 (16)	180	156	145		96.7 (95.3)	42.1	20.0	4.6
	M	—	—	326	204	154		7.40	49 (32)	216	216	185	693	—	33.7	5.9	-20.2
30	1	7.75	600 (408)	320	242	178		5.18	107 (71)	208	167	126		82.2 (82.6)	35.0	31.0	29.2
	2	7.89	584 (388)	297	242	181		5.04	17 (10)	197	179	145		97.1 (97.4)	33.6	26.0	19.9
	M	—	—	308	242	180		7.90	51 (31)	248	220	218		—	19.5	9.1	-21.1
31	1	7.91	621 (437)	272	186	126	632	4.91	18 (14)[d]	144	128	112	686	97.1 (96.8)[d]	47.0	31.2	11.1
	2	8.06	570 (422)	238	186	118		5.23	140 (99)	188	144	52		75.4 (76.5)	21.0	22.6	55.9
	M	—	—	255	186	122		7.42	62 (35)	191	166	170	658	—	25.1	10.8	-39.3
32	1	7.79	502 (374)	239	168	111		5.04	20 (16)	131	120	52		96.0 (95.7)	45.2	28.6	53.2
	2	7.99	346 (248)	209	148	126		5.05	10 (9)	120	100	41		97.1 (96.4)	42.6	32.4	67.5
	M	—	—	224	158	118		7.68	45 (29)	143	122	165		—	36.2	22.8	-39.8
33	1	8.20	466 (309)	226	107	68		5.32	8 (2)	114	82	38		98.3 (99.4)	49.6	23.4	44.1
	2	7.69	494 (371)	238	194	118	703	5.12	12 (6)	134	126	52	659	97.6 (98.4)	43.7	35.0	55.9
	M	—	—	232	150	93		7.50	36 (24)	163	140	150	647	—	29.7	6.7	-61.3

[a] Values in parentheses are volatile suspended solids.

[b] Underscored values are based on average of IPC influent samples.

[c] Composites
  1 – 7:30 a.m. to 7:30 p.m. samples.
  2 – 7:30 p.m. to 7:30 a.m. samples.
  M – Mill composite analyzed in IPC lab.

[d] Sludge carry-over due to failure of sludge pump.

TABLE C-3. CLARIFIER STUDY AT COMBINED LOCKS – FERRIC CHLORIDE (75 mg/1 Fe^{3+}) PLUS NALCOLYTE 73C32 (0.75 mg/1)[a,b]

Day	Composite[c]	Influent (C)						Effluent (D)						% Reduction			
				BOD$_5$, mg/1						BOD$_5$, mg/1					BOD$_5$		
		pH	Sus. Sol., mg/1	Total	Soluble	Color Units	Sol. Sol., mg/1	pH	Sus. Sol. mg/1	Total	Soluble	Color Units	Sol. Sol., mg/1	Sus. Sol.	Total	Soluble	Color
36	1	8.10	424 (292)	220	126	60	551	5.54	4 (3)	106	100	30	630	99.0 (99.0)	51.8	20.6	50.0
	2	7.72	258 (193)	255	152	90		5.26	28 (18)	121	122	90		89.1 (90.7)	52.5	19.7	0
	M	--	--	238	139	--		7.78	41 (30)	142	144	105	633	--	40.3	-3.6	--
37	1)																
	2) Failure of Sludge Pump																
	M)																
38	1	7.99	389 (254)	188	106	98	593	6.30	30 (25)	124	87	138	619	92.3 (90.2)	34.0	17.9	-40.8
	2	8.31	521 (361)	318	238	190		6.57	77 (48)	198	193	108		85.2 (86.7)	37.7	18.9	43.2
	M	--	--	253	172	--		7.89	44 (26)	186	191	195	779	--	26.5	-11.0	--
39	1[d]	8.18	590 (403)	355	266	160		6.70	81 (48)	249	212	93		86.3 (88.1)	29.9	20.3	41.9
	2[d]	8.53	702 (456)	409	286	163		6.80	106 (64)	265	213	85		84.9 (86.0)	35.2	25.5	47.8
	M	--	--	382	276	--		7.85	53 (30)	272	260	233		--	28.8	5.8	--
40	1[d]	7.65	606	314	237	160	819	6.75	81	263	196	105	874	86.6	16.2	17.3	34.4
	2[d]	7.75	431	336	280	160		5.15	130	246	220	83		69.8	26.8	21.4	48.1
	M	--	--	325	258	--		7.48	45	258	240	262	803	--	20.6	7.0	--

[a] Values in parentheses are volatile suspended solids.

[b] Underscored values are based on average of IPC influent samples.

[c] Composites

1 – 7:30 a.m. to 7:30 p.m. samples.
2 – 7:30 p.m. to 7:30 a.m. samples.
M – Mill composite analyzed in IPC lab.

[d] Heavy floc carry-over due to sludge pump troubles.

TABLE C-4. CLARIFIER STUDY AT COMBINED LOCKS — FERRIC SULFATE (100 mg/l Fe^{3+})[a]

		Influent (C)						Effluent (D)						% Reduction			
			Sus. Sol.,	BOD_5, mg/l		Color	Sol. Sol.,		Sus. Sol.,	BOD_5, mg/l		Color	Sol. Sol.,		BOD_5		
Day	Composite[b]	pH	mg/l	Total	Soluble	Units	mg/l	pH	mg/l	Total	Soluble	Units	mg/l	Sus. Sol.	Total	Soluble	Color
44	1	8.80	353	262	223	118	780	4.90	37	177	174	92	663	89.5	32.4	22.0	22.0
	2	7.70	196	304	230	150		4.85	66	194	194	168		66.3	36.2	15.6	-12.0
	M	--	--	283	226	--		7.50	56	219	210	178	788	--	22.6	7.1	—
45	1	7.60	384	292	222	123	848	4.51	10	157	152	75	815	97.4	46.2	31.5	39.0
	1A	7.60	374	252	201	108	743	4.72	87	178	164	108	854	76.7	29.4	18.1	0
	2	5.87	430	304	242	123		3.78	60	166	154	83		86.0	45.4	36.4	35.0
	M	--	--	283	222	--		7.55	65	218	197	168	740	—			
46	1	8.03	408	180	104	50		4.53	14	84	78	38		96.6	53.3	25.0	24.0
	2	8.18	431	150	62	30		4.88	24	54	46	20		94.4	64.0	25.8	33.3
	M	—	—	165	83	—		7.75	43	112	95	55		—	32.1	-14.4	—
47	1	7.62	373	133	81	30		5.02	14	69	66	15		96.2	48.1	18.5	50.0
	2	7.35	337	234	192	115		5.05	22	148	132	98		93.5	36.8	31.2	14.8
	M	—	—	184	136	--		7.12	36	114	108	117		--	38.0	20.6	—

[a] Underscored values are based on average of IPC influent samples.

[b] Composites

1 — 7:30 a.m. to 7:30 p.m. samples
2 — 7:30 p.m. to 7:30 a.m. samples.
M — Mill composite analyzed by IPC lab.

TABLE C-5. CLARIFIER STUDY AT COMBINED LOCKS — ALUM (300 mg/1)[a]

Day	Composite[b]	Influent (C) pH	Influent (C) Sus. Sol., mg/1	Influent (C) BOD₅, mg/1 Total	Influent (C) BOD₅, mg/1 Soluble	Influent (C) Color Units	Effluent (D) pH	Effluent (D) Sus. Sol., mg/1	Effluent (D) BOD₅, mg/1 Total	Effluent (D) BOD₅, mg/1 Soluble	Effluent (D) Color Units	% Removal Sus. Sol.	% Removal BOD₅ Total	% Removal BOD₅ Solubles	% Removal Color
50	1	7.57	436	310	226	168	5.25	29	178	180	113	93.3	42.6	20.4	32.7
	2	N.G.	Sample Pump Failed				5.20	103	202	190	117	—	—	—	—
	M	—					7.23	43	188	170	225	—	—	—	—
51	1	7.42	342	332	226	155	5.23	16	198	195	132	97.0	40.4	13.7	14.8
	1A	7.12	544	332	234	113	4.98	249[c]	216	202	128	54.2[a]	39.2	13.7	-13.3
	2	7.53	488	368	270	208	5.63	26[c]	244	226	295	94.6	38.8	16.3	-41.8
	M	—	—	344	243	—	7.15	49	248	230	348	—	27.9	5.3	—
52	1A	7.59	437	317	242	200	5.35	37	200	197	177	91.5	36.9	18.6	11.5
	1B	7.75	419	336	213	215	10.18	140	180	174	90	66.6	46.4	18.3	58.1
	2	7.62	289	367	296	255	5.20	35	242	246	153	87.9	34.0	16.9	40.0
	M	—	—	340	250	—	7.38	75	284	246	362	—	15.0	2.0	—
53	1	7.86	283	222	166	223	10.00	116	154	140	38	59.0	30.6	15.7	83.0
	2	7.79	293	268	202	168	4.61	24	163	164	145	91.8	39.2	18.8	13.7
	M	—	—	245	184	—	7.72	58	258	218	217	—	-5.0	-18.5	—
54	1	7.65	406	240	165	113	5.51	22	204	200	52	94.6	15.0	-21.2	56.0
	2	7.58	373	272	236	168	6.20	26	236	228	105	93.0	13.2	3.4	37.5
	2A	7.80	181	281	250	168	10.15	147	258	224	62	18.8	8.2	10.4	63.1
	M	—	—	264	217	—	7.51	47	222	216	73	—	15.9	0.5	—

[a] Underscored values are based on average of IPC influent samples.

[b] Composites

1 — 7:30 a.m. to 7:30 p.m. samples
2 — 7:30 p.m. to 7:30 a.m. samples
M — mill composite analyzed by IPC lab.

[c] Heavy floc carry-over due to sludge pump troubles.

TABLE C-6. CLARIFIER STUDY AT COMBINED LOCKS WITH AND WITHOUT ALUM (300 mg/1) PLUS HERCOFLOC 812.3 (0.75 mg/1)[a]

Day	Composite[b]	Influent (C)					Effluent (D)					% Reduction			
		pH	Sus. Sol., mg/1	BOD_5, mg/1 Total	BOD_5, mg/1 Soluble	Color Units	pH	Sus. Sol., mg/1	BOD_5, mg/1 Total	BOD_5, mg/1 Soluble	Color Units	Sus. Sol.	BOD_5 Total	BOD_5 Soluble	Color
57	1	7.76	466	342	256	136	6.11	38	252	234	120	91.8	26.3	8.6	11.8
	2	7.52	446	396	294	192	5.72	40	285	248	156	91.0	28.0	15.6	18.8
	M	—	—	369	275	—	7.45	48	307	276	238	—	16.8	0	—
58	1	7.49	670	308	188	184	6.01	54	185	180	164	91.9	39.9	4.2	10.9
	1A	7.59	495	386	234	172	6.12	118	239	216	200	76.2	38.1	7.7	-16.3
	2	7.52	561	320	210	207	7.29	63	242	218	246	88.8	24.4	-3.8	-18.8
	M	—	—	338	211	—	7.40	56	236	218	254	—	30.2	-3.3	—
	Alum pump failed														
71	1	8.31	1164	553	362	239	7.05	187	383	310	101	83.9	30.7	14.4	57.7
	2	8.32	431	377	276	262	5.21	130	236	228	74	69.8	37.4	17.4	71.8
	M	—	—	467	319	—	7.81	56	320	279	254	—	31.5	12.5	—
72	1	8.60	2340	527	347	234	6.50	70	260	239	106	97.0	50.7	31.1	54.7
	2	8.49	471	372	200	140	7.05	91	230	160	74	80.7	38.2	20.0	47.1
	M	—	—	450	274	—	7.80	76	304	260	212	—	32.4	5.1	—
73	1	8.20	527	272	156	117	7.08	58	122	114	82	89.0	55.1	26.9	29.9
	2	8.32	591	316	115	152	7.20	90	170	141	98	84.8	46.2	-22.6	35.5
	M	—	—	294	136	—	7.58	44	145	131	188	—	50.7	3.7	—

[a] Underscored values are based on average of IPC influent samples.

[b] Composites

1 — 7:30 a.m. to 7:30 p.m. samples.
2 — 7:30 p.m. to 7:30 a.m. samples.
M — Mill composite analyzed by IPC lab.

TABLE C-7. CLARIFIER STUDY AT COMBINED LOCKS — SECOND BASE LINE (GRAVITY SEDIMENTATION AFTER 0.010-INCH SIEVE) WITHOUT ADDITIVES[a]

		Influent (C)					Effluent (D)					% Reduction			
			Sus. Sol.,	BOD5, mg/1		Color		Sus. Sol.,	BOD5, mg/1		Color		BOD5		
Day	Composite[b]	pH	mg/1	Total	Soluble	Units	pH	mg/1	Total	Soluble	Units	Sus. Sol.	Total	Soluble	Color
59	1	7.52	461	246	157	188	7.68	32	154	156	242	93.0	37.4	0.6	-28.7
	2	7.58	717	570	406	500	7.78	52	514	450	656	92.7	9.8	-10.8	-31.2
	M	—	—	408	282	—	7.45	50	312	292	392	—	23.5	-3.5	—
60	1	7.60	571	317	228	238	7.85	57	243	220	328	90.0	23.3	3.5	-37.8
	2	7.60	550	278	219	212	7.87	48	234	191	340	91.3	15.8	12.8	-60.4
	M	—	—	298	224	—	7.63	48	262	200	288	—	12.1	10.7	—
61	1	8.22	519	308	192	152	8.35	69	206	200	200	86.7	33.1	-4.2	-31.6
	2	8.25	520	410	264	204	8.42	60	302	275	278	88.5	26.3	-4.2	-36.3
	M	—	—	359	228	—	8.02	45	234	232	262	—	34.8	-1.8	—
65	1	9.25	654	334	209	106	9.30	81	225	204	152	87.6	32.6	2.4	-43.4
	2	9.13	505	326	204	160	9.12	47	208	202	200	90.7	36.2	1.0	-25.0
	M	—	—	330	206	—	8.75	57	222	200	192	—	32.7	2.9	—
66	1	8.98	478	381	258	172	8.88	44	276	246	230	90.8	27.6	4.6	-33.7
	2	7.85	546	423	261	219	7.93	42	298	250	242	92.3	29.6	4.2	-10.5
	M	—	—	402	260	—	7.85	59	272	234	235	—	32.3	10.0	—
67	1	8.58	523	266	116	152	10.17	38	168	139	164	92.7	36.8	-19.8	-7.9
	2	9.01	476	114	20	82	9.05	25	38	30	82	94.7	66.7	-50.0	0
	M	—	—	190	68	—	8.50	52	114	90	152	—	40.0	-32.4	—
68	1	9.14	555	165	12	50	8.90	3	36	32	50	99.4	78.2	-166.6	0
	M	—	—	—	—	—	8.75	30	63	38	82	—	—	—	—

[a] Underscored values are based on average of IPC influent samples.

[b] Composites
1 — 7:30 a.m. to 7:30 p.m. samples
2 — 7:30 p.m. to 7:30 a.m. samples
M — Mill composite analyzed by IPC lab.

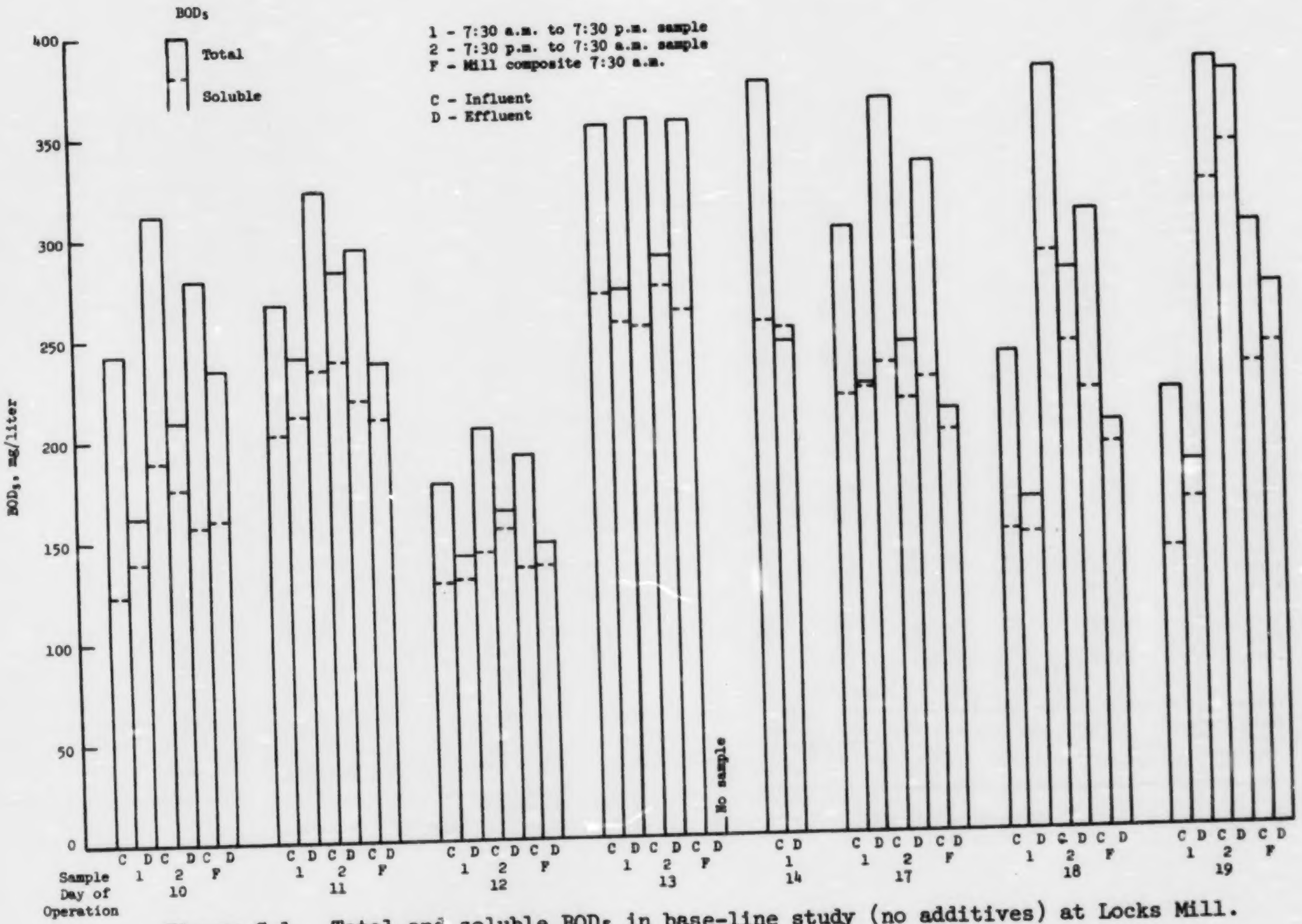

Figure C-1. Total and soluble BOD_5 in base-line study (no additives) at Locks Mill.

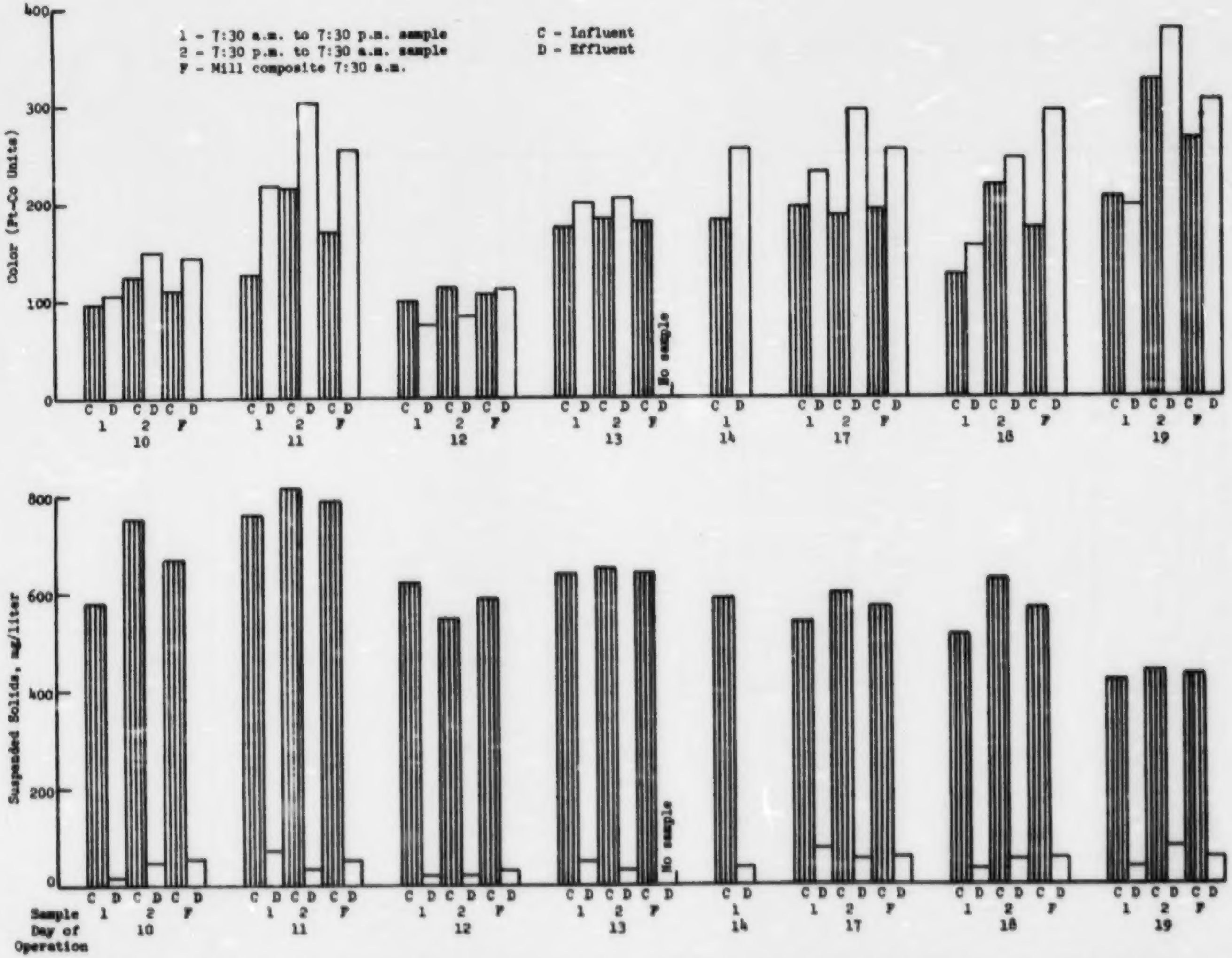

Figure C-2. Color and suspended solids in base-line study (no additives) at Locks Mill.

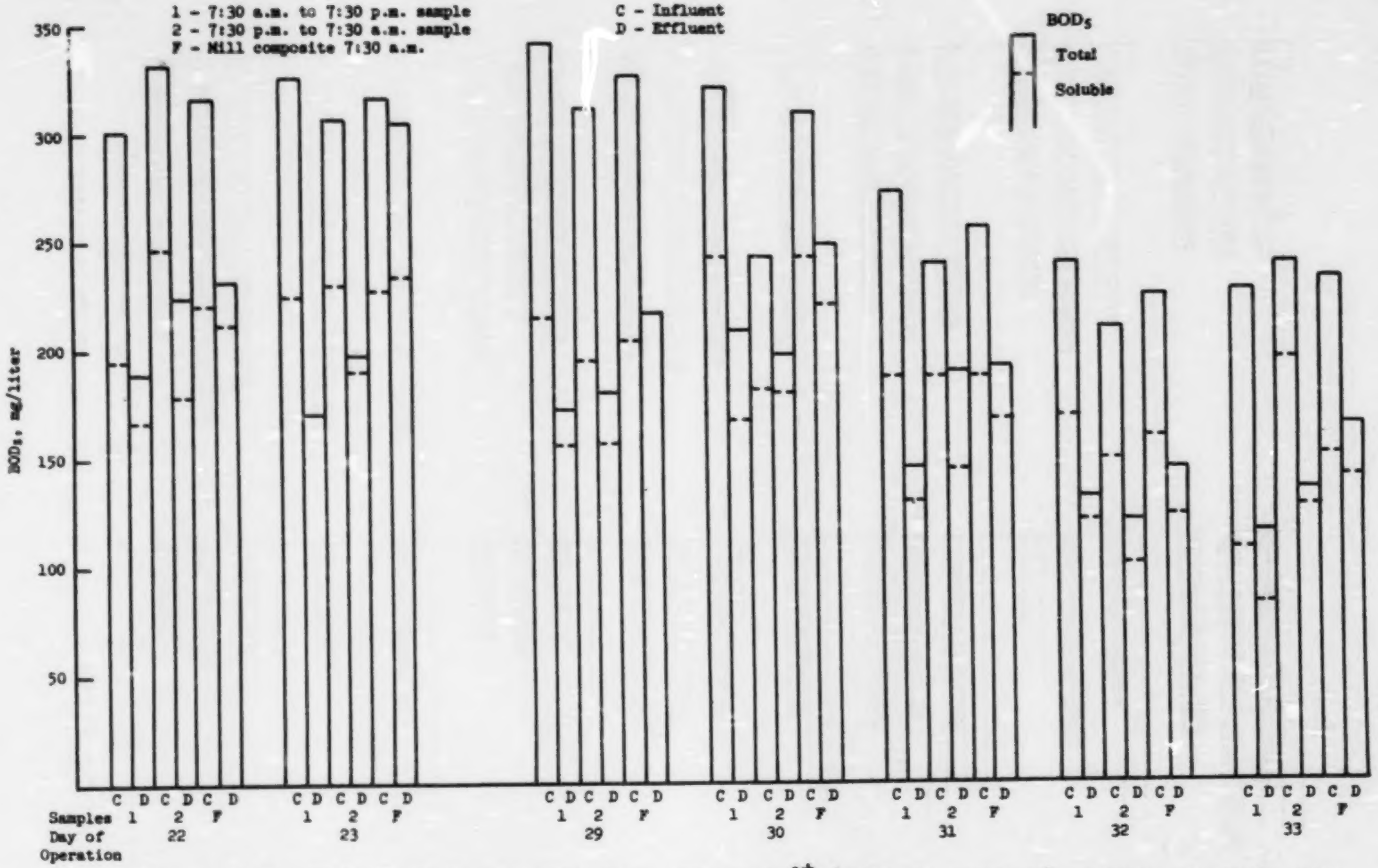

Figure C-3. Effect of ferric chloride — 75 mg Fe^{3+} (without polymer) on BOD$_5$ at Locks Mill.

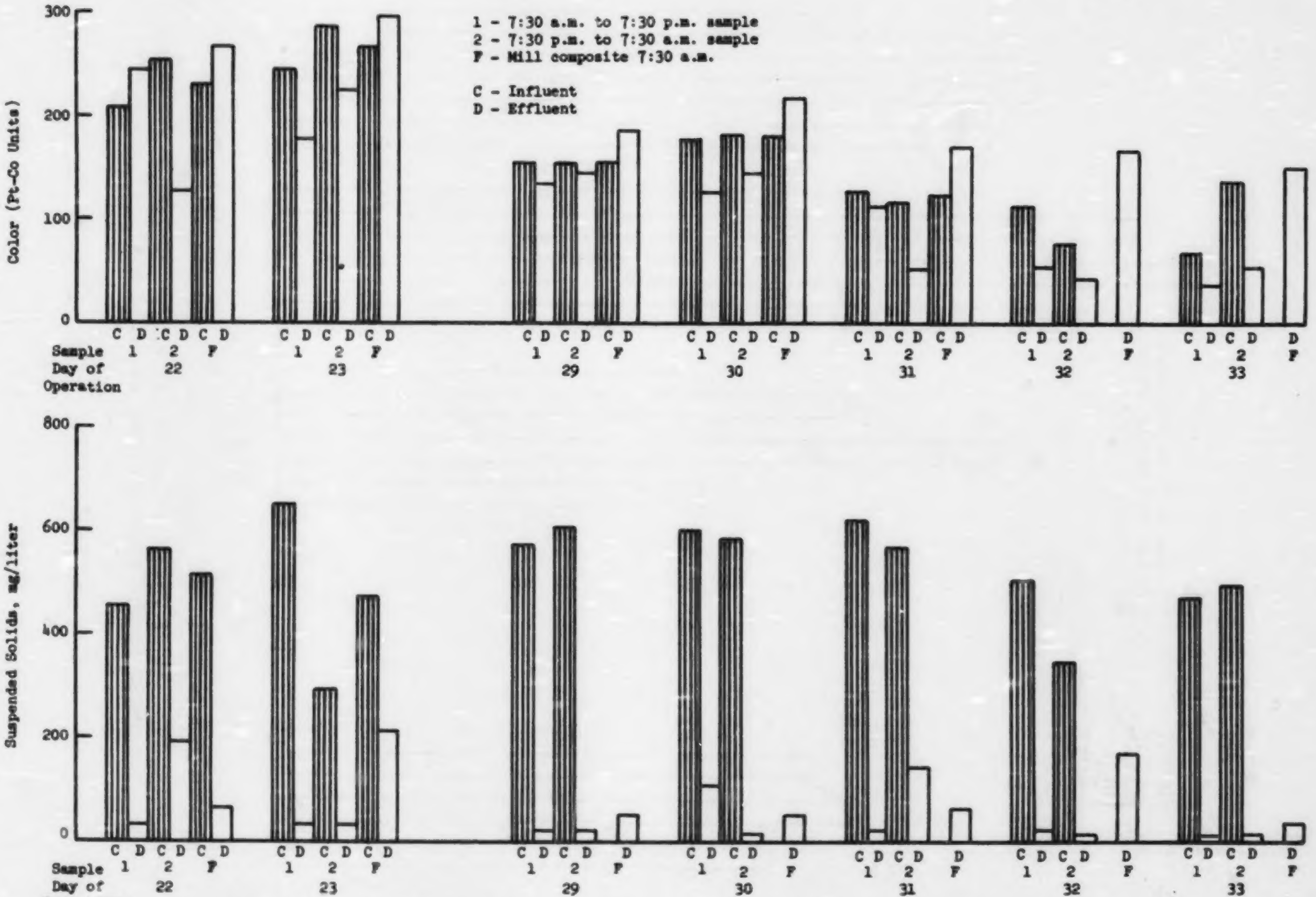

Figure C-4. Effect of ferric chloride — 75 mg Fe^{3+} (without polymer) on color and suspended solids at Locks Mill.

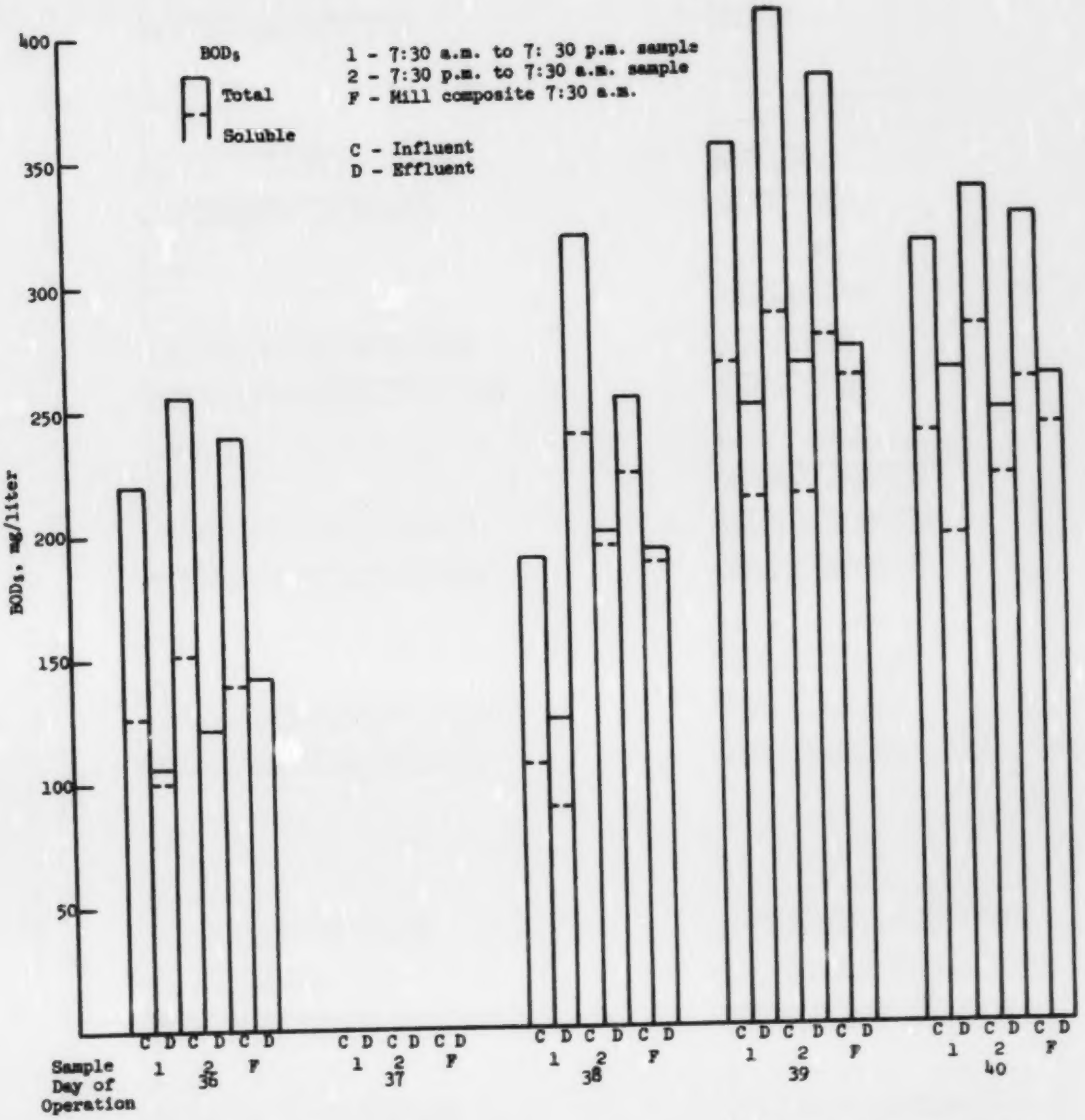

Figure C-5. Effect of ferric chloride (75 mg Fe^{3+}/liter) + Nalcolyte 73C32 (1 mg/liter) on BOD_5 at Locks Mill.

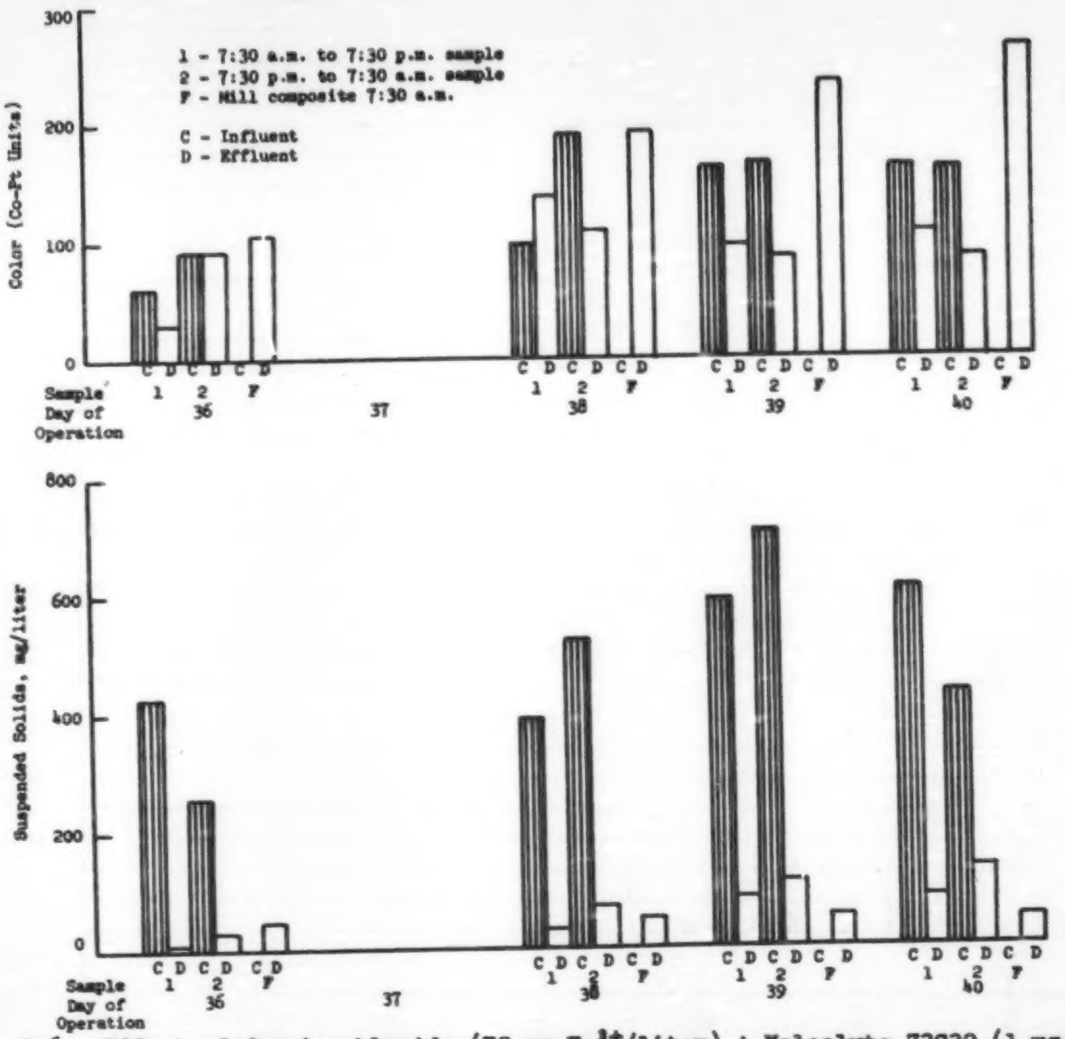

Figure C-6. Effect of ferric chloride (75 mg Fe^{3+}/liter) + Nalcolyte 73C32 (1 mg/liter) on color and suspended solids at Locks Mill.

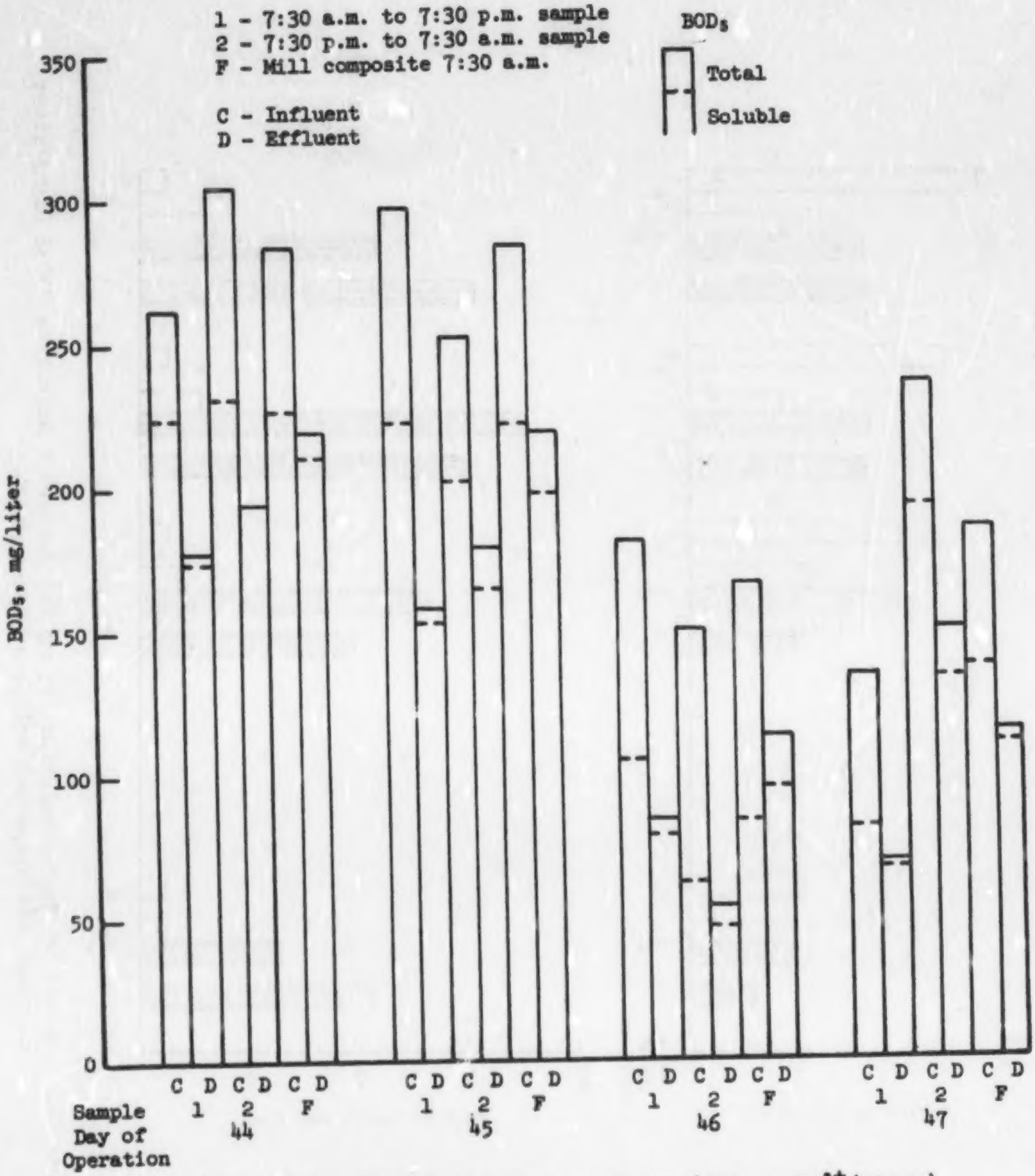

Figure C-7. Effect of ferric sulfate (100 mg Fe^{3+}/liter) on BOD_5 at Locks Mill

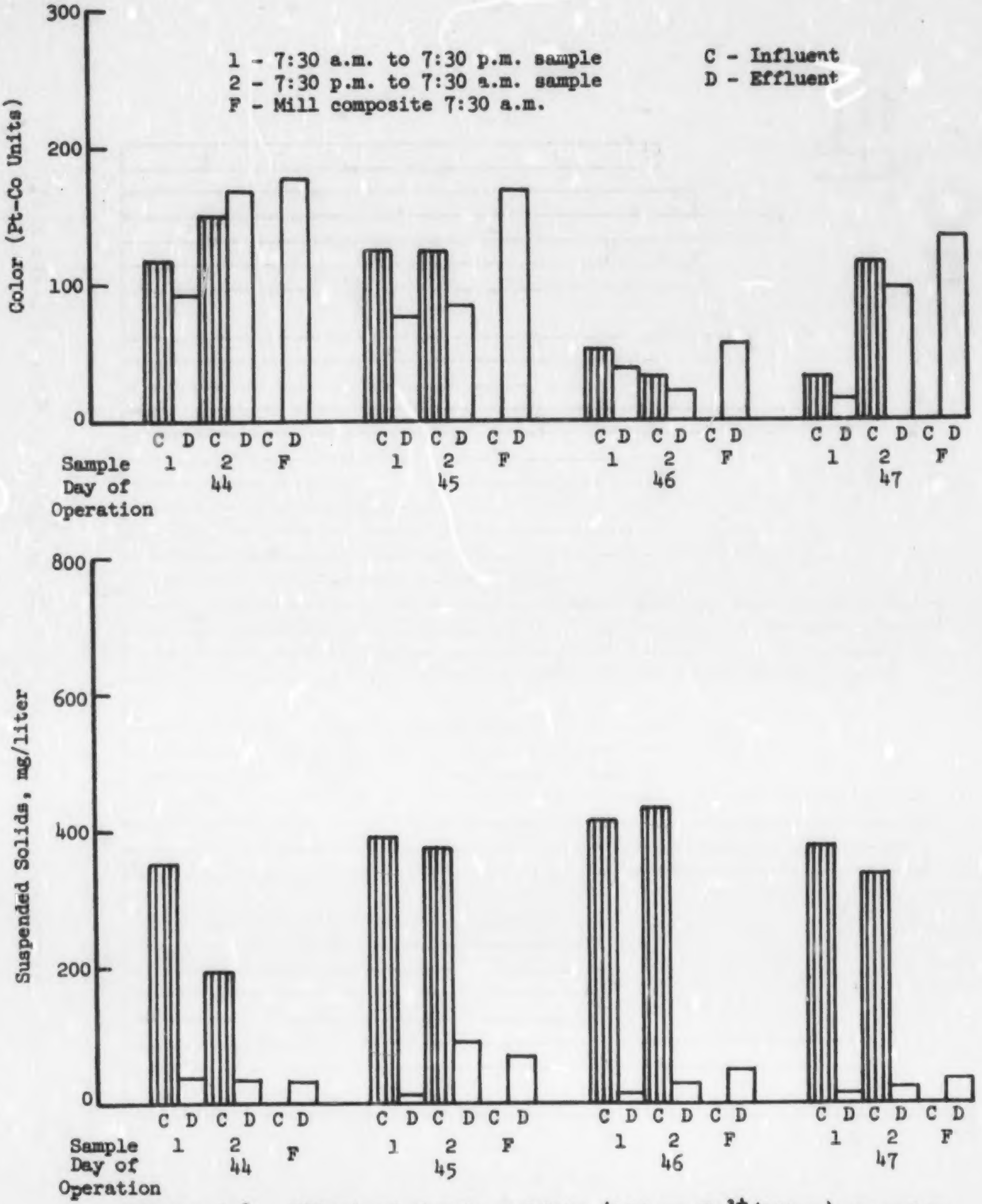

Figure C-8. Effect of ferric sulfate (100 mg Fe^{3+}/liter) on color and suspended solids at Locks Mill.

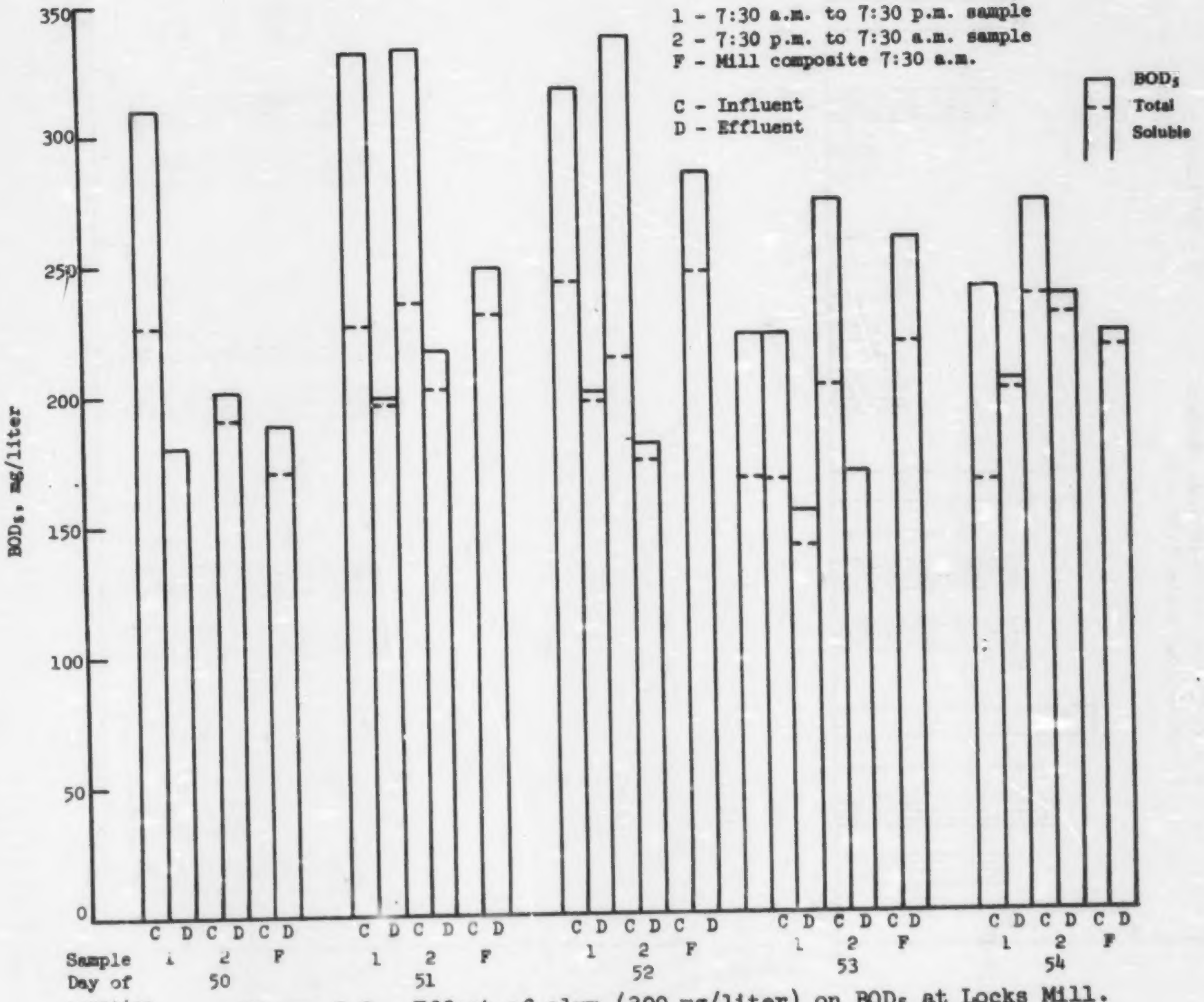

Figure C-9. Effect of alum (300 mg/liter) on BOD$_5$ at Locks Mill.

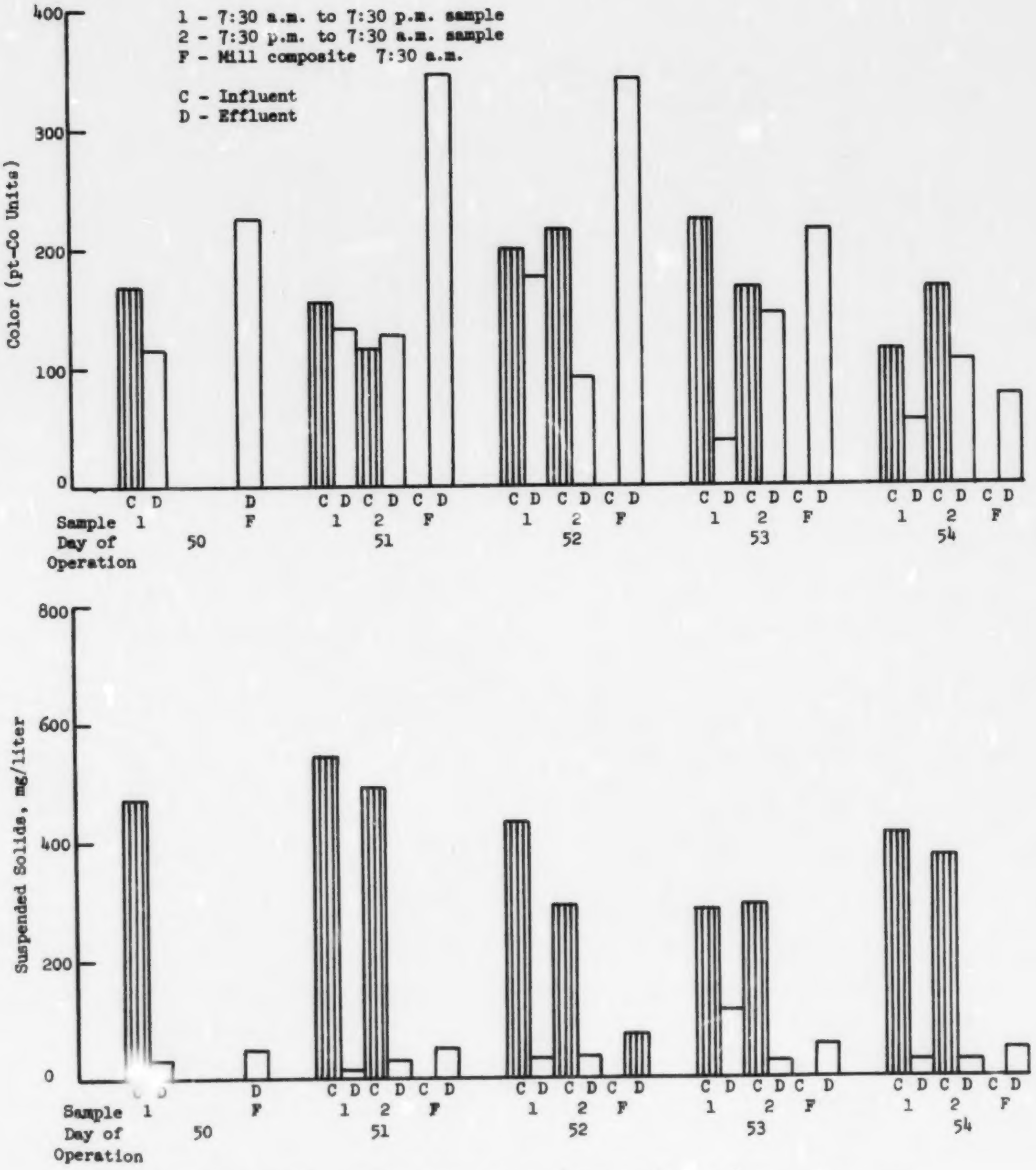

Figure C-10. Effect of alum (300 mg/liter) on color and suspended solids at Locks Mill.

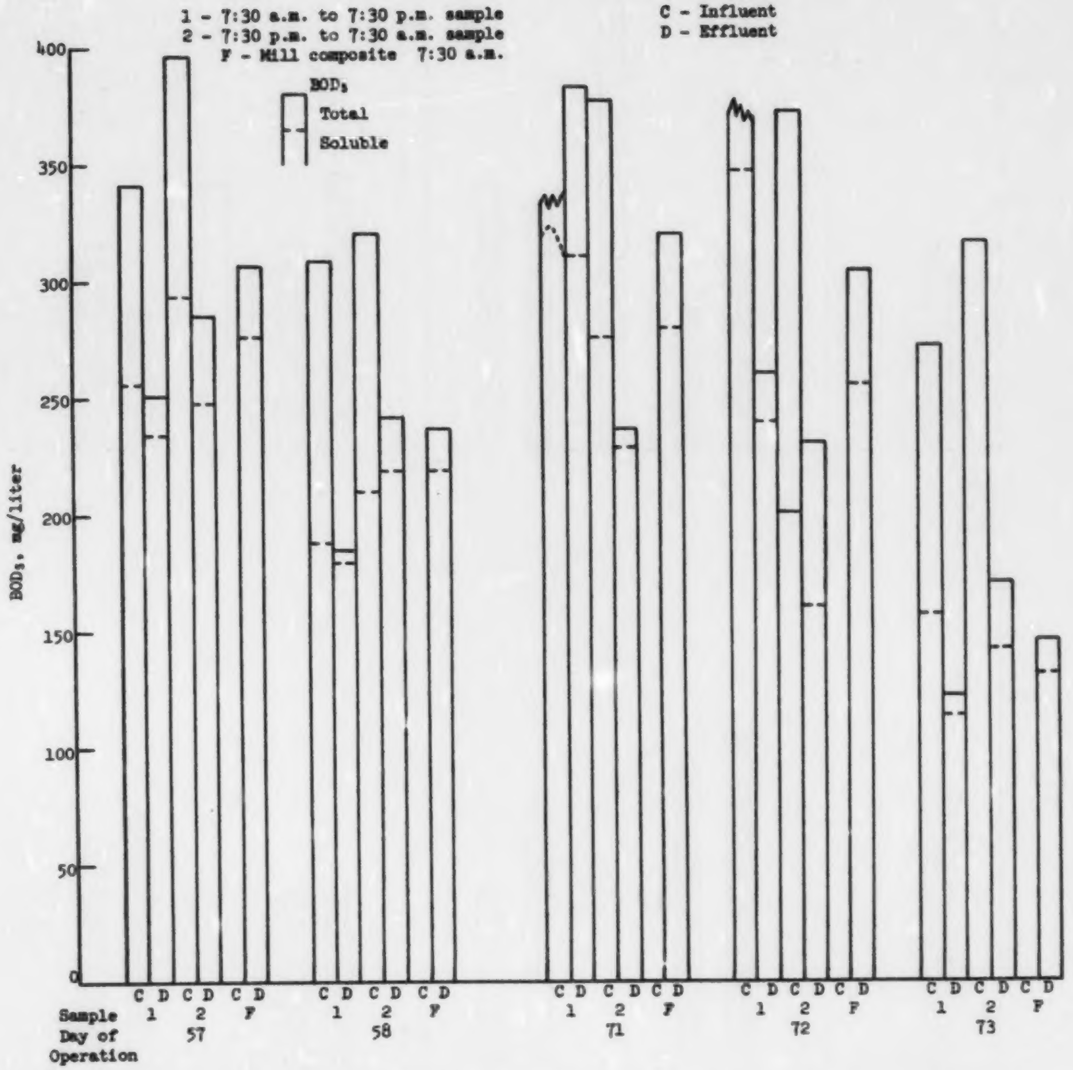

Figure C-11. Effect of alum (300 mg/liter) + Hercofloc 812.3 (0.75 mg/liter) on BOD$_5$ at Locks Mill.

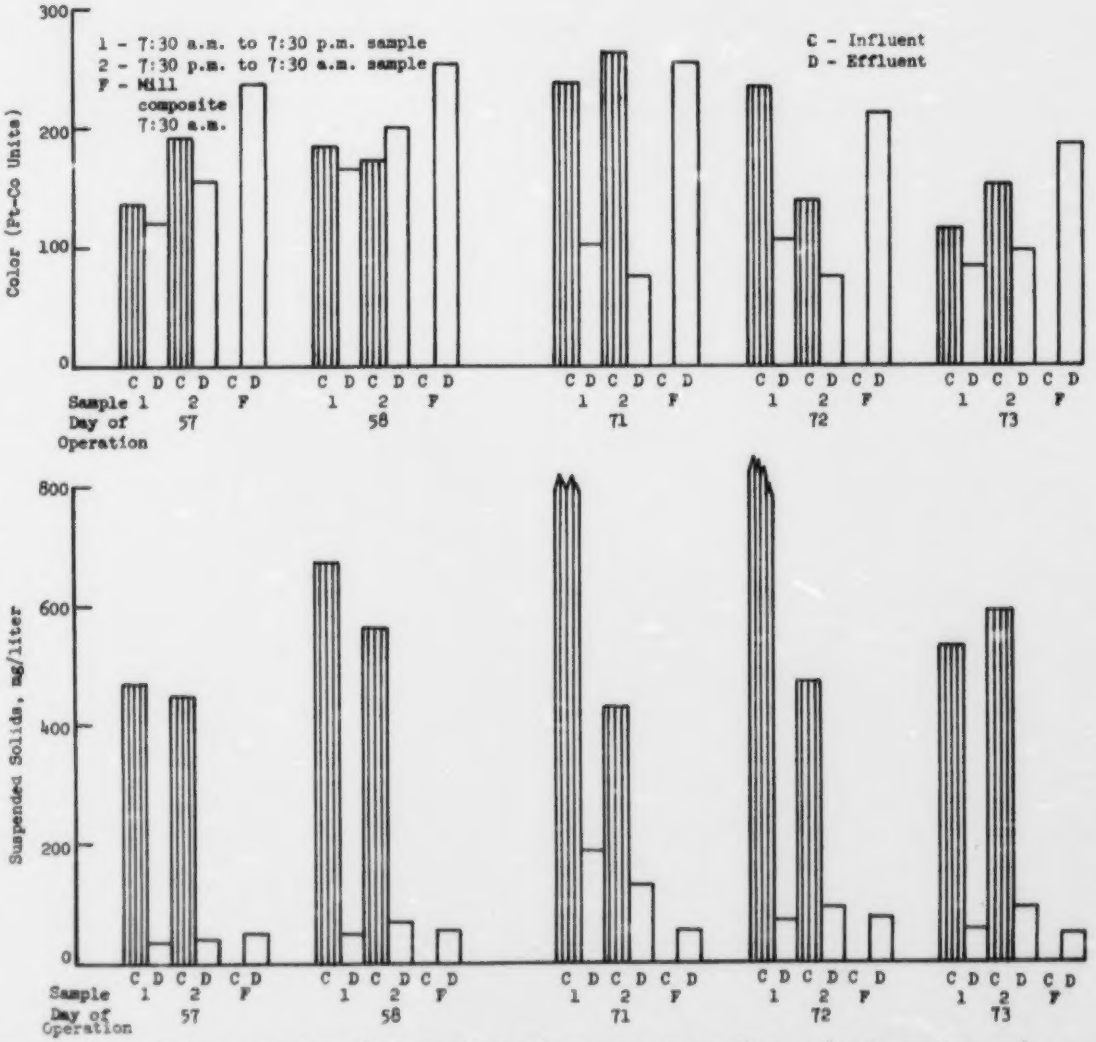

Figure C-12. Effect of alum (300 mg/liter) + Hercofloc 812.3 (0.75 mg/liter) on color and suspended solids at Locks Mill.

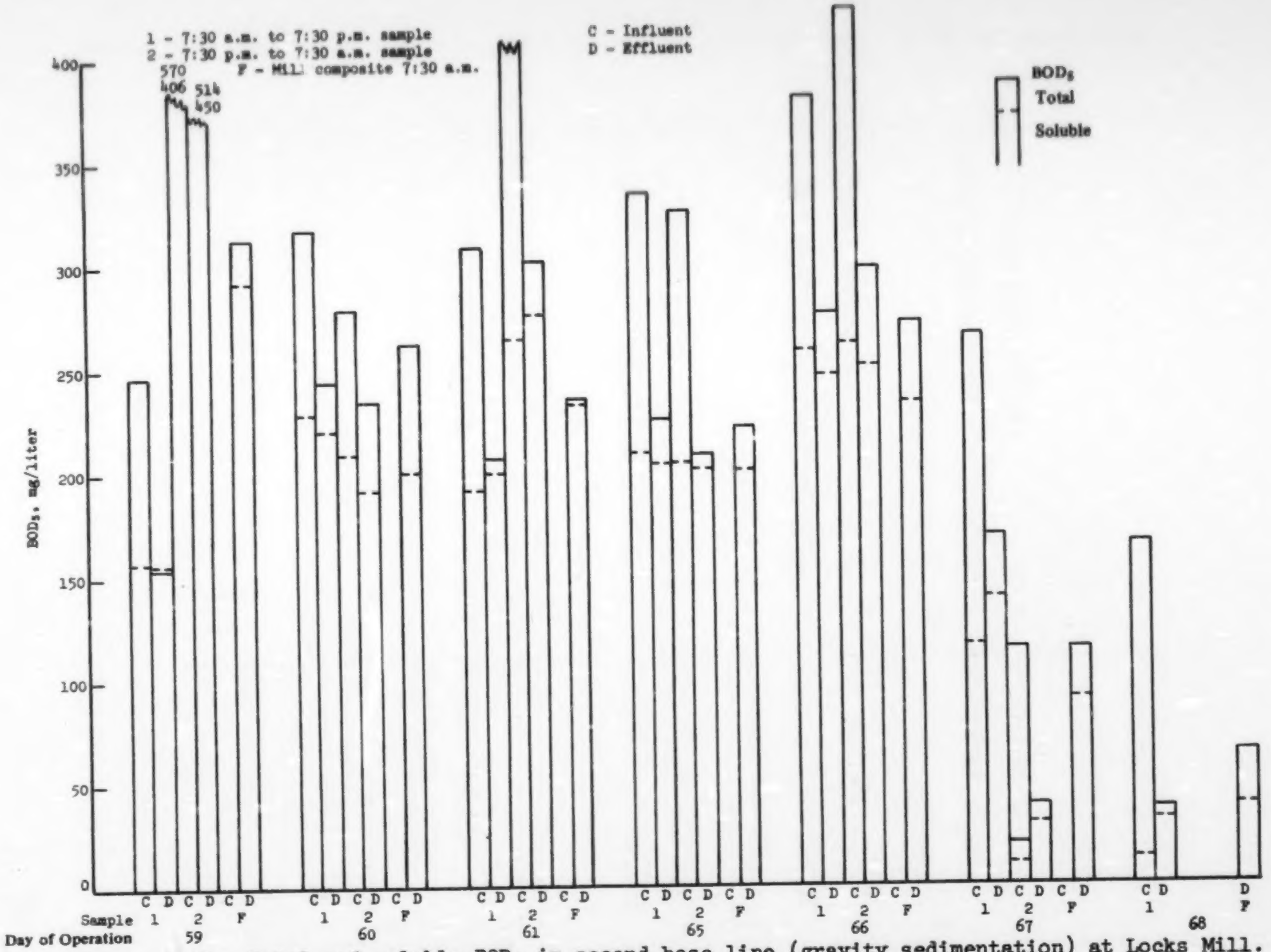

Figure C-13. Total and soluble BOD$_5$ in second base line (gravity sedimentation) at Locks Mill.

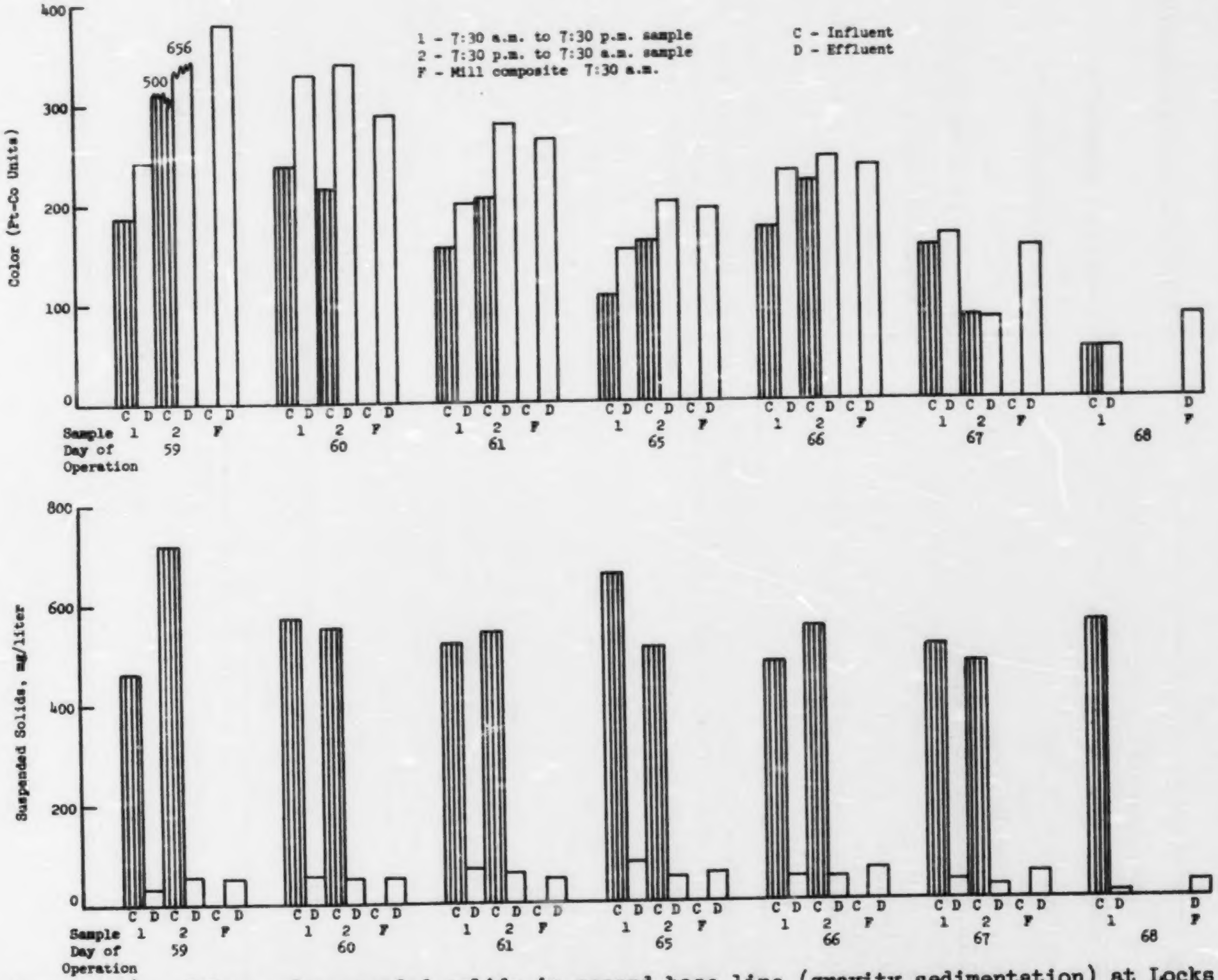

Figure C-14. Color and suspended solids in second base line (gravity sedimentation) at Locks Mill.